

Attorney Docket No.: P-3724-2-F1-C2 (SLD 2 0035-3-3-1-1(II))

RECEIVED JUN 20 MAIL ROOM

SUPPLEMENTAL APPLICATION DATA SHEET

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Application Information

Title Line One::

IMPROVED MULTI-LAYER GOLF BALL

Total Drawing Sheets::

1

Formal Drawings?::

Yes

Application Type::

Utility

Page 1

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41,463

Page 2

Continuity Information

This application is a:: > Application One:: Filing Date::

which is a::
>> Application Two::
Filing Date::

which is a:: >>> Application Three:: Filing Date::

which is a::
>>>Application Four::
Filing Date::

Continuation of
U.S. Serial No. 08/870,585
June 6, 1997

Abanchond
File Wrapper Continuation of
U.S. Serial No. 08/556,237

November 9, 1995

Continuation-in-Part of
U.S. Serial No. 08/542,793

October 13, 1995

Continuation-in-Part of
U.S. Serial No. 08/070,510

June 1, 1993

abandoned

Prior Foreign Applications

Foreign Application One:: Filing Date:: Country:: Priority Claimed:: (Y or N)

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Walnington, D.C. 20231
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.	
09/832,154	04/10/2001	Michael J. Sullivan	P-3724-2-F1-C2	2656	
# 7 17 PP	90 12/18/2001		,		
MICHELLE E	BUGBEE, ASSOCIAT	EXAMINER			
SPALDING SP 425 MEADOW	ORTS WORLDWIDE I	NC	GORDON,	RAEANN	
PO BOX 901			ART UNIT	PAPER NUMBER	
Сисорее, м	A 01021-0901		3711		
			DATE MAILED: 12/18/200	1	

Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 07-01)

A		Application No.	Applicant(s)
	 /	09/832,154	MICHAEL J. SULLIVAN
	Office Action Summary	Examiner	Art Unit
		Raeann Gorden	3711
Period for			
THE N - Extens after S - If the - If NO - Failum - Any re	PRIENED STATUTORY PERIOD FOR REPLY INITIAL ING DATE OF THIS COMMUNICATION. Is sions of time may be available under the provisions of 37 CFR 1.1 SIX (6) MONTHS from the mailing date of this communication. Deriod for reply specified above is less than thirty (30) days, a reply period for reply is specified above, the maximum statutory period to to reply within the set or extended period for reply will, by statute ply received by the Office later than three months after the mailing dipatent term adjustment. See 37 CFR 1.704(b).	36(a). In no event, however, may a reply be the within the statutory minimum of thirty (30) day will apply and will expire SIX (6) MONTHS from cause the amplication to become ABANDON!	mely filed ys will be considered timely. the mailing date of this communication. ED (35 U.S.C. § 133).
1)⊠	Responsive to communication(s) filed on 102	<u> April 2001</u> .	
2a)□	***************************************	nis action is non-final.	
3)	Since this application is in condition for allow closed in accordance with the practice under	ance except for formal matters, p Ex parte Quayle, 1935 C.D. 11,	prosecution as to the merits is 453 O.G. 213.
Dispositi	on of Claims		
4)🛛	Claim(s) 1-6 is/are pending in the application.		
	4a) Of the above claim(s) is/are withdra	wn from consideration.	
5)[Claim(s) is/are allowed.		
6)⊠	Claim(s) 1-6 is/are rejected.		
7)	Claim(s) is/are objected to.		
8)	Claim(s) are subject to restriction and/o	or election requirement.	
	ion Papers		
9)	The specification is objected to by the Examin	er.	
10)	The drawing(s) filed on is/are: a)☐ acce	epted or b)□ objected to by the Ex	raminer.
	Applicant may not request that any objection to the	he drawing(s) be held in abeyance.	See 37 CFR 1.85(a).
11)	The proposed drawing correction filed on	_ is: a)∏ approved b)∏ disapp	proved by the Examiner.
	If approved, corrected drawings are required in re	eply to this Office action.	
12)	The oath or declaration is objected to by the E	xaminer.	
	under 35 U.S.C. §§ 119 and 120		
13)[Acknowledgment is made of a claim for foreign	gn priority under 35 U.S.C. § 119	(a)-(d) or (f).
a)	☐ All b)☐ Some * c)☐ None of:		
	1. Certified copies of the priority document		
	2. Certified copies of the priority document		
*	Copies of the certified copies of the pri application from the International E See the attached detailed Office action for a list	Bureau (PC) Rule (7.2(a)).	
14)	Acknowledgment is made of a claim for dome	stic priority under 35 U.S.C. § 11	9(e) (to a provisional application).
	 a) The translation of the foreign language p Acknowledgment is made of a claim for dome 	rovisional application has been i	received.
Attachme	nt(s)		
2) Not	ice of References Cited (PTO-892) lice of Draftsperson's Patent Drawing Review (PTO-948) ormation Disclosure Statement(s) (PTO-1449) Paper No(s	5) Notice of Inform	nary (PTO-413) Paper No(s) nal Patent Application (PTO-152)
<u> </u>	Trademark Office		

U.S. Patent and Trademark Office PTO-326 (Rev. 04-01) Application/Control Number: 09/832,154

Art Unit: 3711

Page 2

DETAILED ACTION

Double Patenting

The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. See *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970);and, *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the conflicting application or patent is shown to be commonly owned with this application. See 37 CFR 1.130(b).

Effective January 1, 1994, a registered attorney or agent of record may sign a terminal disclaimer. A terminal disclaimer signed by the assignee must fully comply with 37 CFR 3.73(b).

Claims 1-6 are rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-8 of U.S. Patent No. 6,210,293. Although the conflicting claims are not identical, they are not patentably distinct from each other because the claimed subject matter is very similar. The present invention claims a golf ball comprising a core, an inner cover, and an outer cover. The inner cover has a Shore D hardness of 60 or more and is made from a blend of two or more low acid ionomer resins containing no more than 16% by weight of an alpha, beta-unsaturated carboxylic acid. The outer cover layer has a Shore D hardness of 64 or less and is made from a polyurethane or non-ionomeric thermoplastic and thermosetting elastomers. The '293 patent claims a golf ball with identical layers and features except the optional non-ionomeric thermoplastic and thermosetting elastomer materials for the

Application/Control Number: 09/832,154

Art Unit: 3711

Page 3

outer cover layer. However, the present invention and the '293 patent both claim a polyurethane outer cover. Claiming additional materials for the outer layer does not render a patentable distinction. One skilled in the art would have included optional materials for the outer cover layer to increase manufacturing flexibility.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Raeann Gorden whose telephone number is 703-308-8354. The examiner can normally be reached on 7:30 AM to 5:00 PM Mon-Fri.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Paul Sewell can be reached on 703-308-2126. The fax phone numbers for the organization where this application or proceeding is assigned are 703-305-3579 for regular communications and 703-308-3579 for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is 703-308-1148.

rg December 13, 2001 Mark S. Graham Primary Examiner

Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

U.S. Patent and Trademark Office PTO-892 (Rev. 01-2001)

4

Notice of References Cited

Part of Paper No. 4



PATENT

TECHNOLOGY CENTER R37(

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RE APPLICATION OF

Michael J. Sullivan

FOR

IMPROVED MULTI-LAYER GOLF BALL

SERIAL NO.

09/832,154

FILED

April 10, 2001

EXAMINER

Raeann Gordon

ART UNIT

3711

ATTORNEY DOCKET NO.

SLD 2 0035¥3-3-1-1(II) / P-3724-2-F1-C2

June 17, 2002

Cleveland, OH 44114-2579

INFORMATION DISCLOSURE STATEMENT

Assistant Commissioner of Patents Washington, D.C. 20231

Dear Sir:

In accordance with 37 C.F.R. §§ 1.56, 1.97, 1.98 and MPEP § 609, applicant submits the following Disclosure Statement concerning art of which the applicant is aware. A copy of PTO-1449 is enclosed herewith.

This Information Disclosure Statement is not intended to constitute an admission that any patent, publication or other information referred to herein or submitted herewith is "prior art" for this invention unless specifically designated as such.

In accordance with 37 C.F.R. §1.97(g) and (h), the filing of this Information Disclosure Statement shall not be construed to mean that a search has been made or that no other material information as defined in 37 C.F.R. §1.56(b) exists.

CERTIFICATE OF MAILING

I hereby certify that this INFORMATION DISCLOSURE STATEMENT is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner of Patents, Washington, D.C. 20231, on June 17, 2002.

By June 17, 2002.

Date: 06-17-02

U.S. Serial No.09/832,154 Attorney Docket No. SLD 2 0035-3-3-1-1(11)

Under § 1.98(a)(3), no concise explanation of relevance is required for information that is in the English language. Accordingly, the enclosed patent requires no further explanation (or no translation is available).

Consideration of the appropriate paragraph(s) indicated below is respectfully requested:

[]	WITHIN	THREE	MONTHS	OF	FILING:	Under	§	1.97(b)(1),	this	information	disclosure
stateme	nt is bein	g filed wit	thin three m	onth	s of the fill	ng date	of	the applica	tion.	Although it	is believed
no fee	is necess	ary, any	deficiency	in fe	es should	be char	ge	d to Deposi	t Acc	ount No. 06	-0308.

BEFORE FIRST OFFICE ACTION: Under § 1.97(b)(3), this information disclosure statement [] is being filed before the mailing date of a first Office Action on the merits. Although it is believed no fee is necessary, any deficiency in fees should be charged to Deposit Account No. 06-0308.

FOREIGN SEARCH REPORT: Under § 1.97(e)(1), the undersigned certifies that each item of [] information contained in this information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of this statement. Although it is believed no fee is necessary, any deficiency in fees should be charged to Deposit Account No. 06-0308.

BEFORE FINAL ACTION/WITH FEE: Under § 1.97(c)(2), this information shall be considered if X filed before the mailing date of a final action if accompanied by a fee in the amount of \$180.00 as required by §1.17(p). Accordingly, the necessary fee accompanies this information disclosure statement. Any overpayment or deficiency can be charged to Deposit Account No. 06-0308.

It is respectfully requested that the attached document(s) be considered and officially cited in examination of this application.

Respectfully submitted,

FAY, SHARPE, FAGAN, MINNICH & McKEE, LLP

Richard M. Klein Reg. No.33,000

1100 Superior Avenue, Seventh Floor Cleveland, Ohio 44114-2518

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TECHNOLOGY CENTER R3700

N-151 DI2D035\3B1BY\LSK0278A.WPD

PATENT SPECIFICATION



Application Date: May 26, 1937. No. 14581 / 37.

494.031

Complete Specification Left: March 22, 1938.

Complete Specification Accepted: Oct. 19, 1938.

TO NOT TEST

PROVISIONAL SPECIFICATION

Improvements in Games Balls and their Manufacture

We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 32, Osnaburgh Street London, N.W.1, Douglas Frank Twiss, Samuel Graham Ball and John 5 Francis Cookson, all British subjects of the aforesaid Company's Works at Fort Dunlop, Erdington, Birmingham, in the County of Warwick, do hereby declare the nature of this invention to be as follows:-

This invention concerns improvements in games balls and their manufacture and especially concerns improvements in the manufacture of golf balls.

Commonly such a ball consists of a 15 cover of india rubber, gutta-percha, balata or the like or an admixture of these which is moulded on to a core, which core may have been wound with strips or threads, for example of rubber, to create 20 a spherical or substantially resilient nucleus.

The objects of the present invention include the provision of a ball of reduced cost in manufacture and offering an in-25 creased resistance to deterioration when subjected to climatic variations or scaking in water and with improved mechanical qualities such as durability against cutfing or abrasion.

It has already been proposed to form covers of various substances such as nitro cellulose and fatty acids or fats, or to form them of cork with a casein binder or from gutta-percha or rubber reinforced 35 with a colloidal material such as glue.

The use of viscose has also been proposed and gutta-percha with or without vegetable resins, viscose or proteins has

been suggested.
According to this invention a games ball such as a golf ball is formed or consists wholly or partly of a water resistant synthetic plastic substance or substances which may incorporate natural or arti-45 ficial rubber and/or gutta-percha and/or balata in suitable proportions.

The said substance or substances may be of any suitable type, but we find those classes of synthetic plastic substances to 50 be most useful which are obtainable by polymerisation of substituted ethylene compounds.

compounds include polyvinyl Such

acetate, polyvinyl chloride, polyvinyl cyanide, poly-styrene or polymerisation 55 products of vinylethylene, or of substitution derivatives of any of the foregoing such as vinylchlorethylene or methylvinyl cyanide.

Compositions containing one or more of 60 these synthetic plastic substances may constitute one or more layers or coatings providing a shell or cover for the ball or

for the core of a golf ball.

Alternatively, the composition com- 65 prising such synthetic plastic materials may constitute the whole or the major part of the ball.

If the composition is to contain rubber, gutta-percha, or balata mixing may be 70 effected in any convenient manner, e.g. by milling together the constituents in a plasticised or powdered condition or by using all or any of the constituents in the form of dough or solution or emulsions or 75 by a combination of such devices, any solvent and/or non-solvent liquid being removed eventually.

Such compositions may be compounded in any desirable manner as for instance, to render them susceptible of being shaped and/or vulcanised, the two processes in the former case occurring either concurrently or as successive operations.

Improvement in the qualities of games 85 balls incorporating such compositions may be effected uniformly throughout the mass of the composition or may be intensified at or adjacent to the surface of the external layer.

Local or uniform hardening, for example, may be effected by heat treatfor. ment with or without concurrent moulding and/or vulcanisation, or by acid treatment of the surface with acids of the 95 sulphonic group, especially sulphuric acid, or by other chemical agents such as formaldehyde.

Fillers such as wood flour may be incorporated in the composition to increase 100 its toughness and suitable pigments such : as titanium white to impart the desired

colour and opacity.

Dated this 25th day of May 1937.

W. BOND, Acting for the Applicants.

COMPLETE SPECIFICATION

Improvements in Games Balls and their Manufacture

We. Dunlop Rubber Company Limited, a British Company of 32, Osnabugh Street, London, N.W.1, Douglas Frank Twiss, Samuel Graham Ball and John Francis Cookson, all British Subjects and all of the aforesaid Company's Works at Fort Dunlop, Erdington, Birming-ham, in the County of Warwick, do hereby declare the nature of this invention 10 and in what manner the same is to be performed, to be particularly described and ascertained in and by the following state-

ment:

This invention concerns improvements 15 in games balls and their manufacture and especially concerns improvements in the manufacture of golf balls, in its applica-tion to which the invention is more parti-

-cularly described.

20. Commonly such a ball consists of a cover of india-rubber, gutta percha, or balata or an admixture of these, which is moulded onto a core which core may be wound with strips or threads, for example 25 of rubber, to create a spherical or sub-stantially spherical resilient nucleus.

It has already been proposed to form covers of various substances such as nitrocellulose and fatty acids or fats, or to form 30 them of cork with a casein binder or from gutta percha or rubber reinforced with a colloidal material such as glue.

The use of viscose has also been proposed and gutta percha with or without vege-35 table resins, viscose, or proteins has been

suggested.

When gutta percha is used alone it is sometimes found to have insufficient resistance to change of temperature more 40 particularly to rise of temperature, whereas by the present invention we are able to impart the desired degree of heat resistance and to prevent deterioration in colour and/or other physical characteristics 45 when subjected to climatic variations or to soaking in water, while imparting improved mechanical qualities such nical qualities such against cutting

durability. abrasion.

We are aware that it has already been proposed to form compositions suitable for golf ball covers from emulsions or dispersions comprising rubber, gutta percha, balata or similar vegetable resins occurring naturally or artificially obtained, and in vulcanised or unvulcanised condition, and that it has also been proposed to use as alternatives or admixtures, aqueous dispersions of congulated rubber, vulcan-60 ised rubber, synthetic or artificial rubber, or rubber-like substances.

The resistance, however to humid atmosphere, to immersion in water and to wet conditions generally, of golf balls produced from the above compositions is liable to be impaired by the inclusion of substances commonly employed as protec-tive colloids for such aqueous dispersions or emulsions which colloids are generally hydrophilic substances with an affinity for water.

In contradistinction thereto golf ball covers when produced by the process as defined below possess to a marked degree the desired feature of resistance to water combined with the absence of any undesirable degree of plasticity at lowered tem-

peratures According to this invention a process for the production of games balls comprises forming the outer portion at least of said balls of a non-aqueous mixture of gutta percha and a water resistant syn-thetic thermoplastic substance comprising a polymerisation product of a member of the vinyl group or of a substitution derivative thereof.

By the term "gutta percha" through-out the specification and claims, we intend By the term "

to include also balata.

The preferred kinds of synthetic thermoplastic substances employed are those products obtained by the polymerisation of chemical substances of the vinyl group that is, containing the grouping CH₂: CH in which the free valency of the second carbon atom is satisfied by a halogen, carboxy-ester, or hydrocarbon radical, for example, vinyl benzene (styrene), vinyl acetate, vinyl-formic 100 (acrylic) esters, vinyl chloride and vinyl cyanide, and halogen or alkyl derivatives of these, such as a vinyl a chlorethylene or a methylvinyl cyanide.

As shown in the accompanying examples, the cover of the ball is comaccompanying 105 posed of a major proportion of gutta percha as for instance, in three parts by weight with which is incorporated a proportion as for instance, one part by weight 110 of one or more of the above substances, and if desired the whole of the ball may be moulded therefrom.

The gutta percha and said substance or substances may be mixed together in any 115 convenient manner, for example by milling together the constituents in a plasticized or powdered condition, or by using all or any of the constituents in the form of dough, or solution, in a non-aqueous 120 solvent, any solvent being removed sub-sequently.

EXAMPLE 1. Three mixtures of the following parts by weight as shown under "A", "B"

and "C", are made on the mixing mills under similar conditions.

		" A "	"B"	" C "
	Deresinated gutta percha	73.325	73.325	73.325
	Polymerised a vinyl-a chlorethylene		22.05	
	Polymerised vinyl-ethylene	•		22.05
10	Pale crepe rubber	22.05		
	Titanium dioxide ,	4.5	4.5	4.5
	Magnesium oxide		1.10	-
	Zinc oxide		2.205	
	Sulphur	0.125	0.125	0.125

From each of these mixtures are formed by a preliminary moulding operation pairs of hemispherical shells which are applied to prepared golf ball cores to which they are moulded in the usual manner, the 20 heating required being 15 minutes at 175° F. The balls so formed when tested by an apparatus for the measurement of the degree of cutting equivalent to a "topped" blow showed a greater 25 resistance to cutting on the part of com-position "C" than either of the other two, and a greater resistance by composi-tion "B" than composition "A".

EXAMPLE 2.

Three compositions "D", "E", 80
"F", composed of parts by weight as shown in the accompanying table are prepared on the mixing mills under similar conditions. On testing the relative resistance of these mixtures to rise of temperature, their relative behaviour is indicated below by the "softening temperature" at which each attained a standard degree of advanced softening. standard degree of advanced softening. The form of the apparatus used being that 40 described in the Journal of the Society of Chemical Industry, 1919, page 405 T.

					D	E)	.E
	Gutta percha -	-	_	-	100	80	73.325
45	Polymerised a vinyl-a cl	hlor	ethyl	ene	-		22.05
	Polyvinyl acetate -	-	-	-		20	
	Titanium dioxide -	-	-	-			4.5
	Magnesium oxide -	_	•	-			2.205
	Zinc oxide		-	-			2.205
50	Sulphur	_	-	-			0.125
•••	Softening temperature	_	-	**	95° C.	115° C.	175° C.

" Th "

It will be seen from the above that the composition marked "F" which is substantially the same as that designated "B" in Example 1, and also composition "E", offer a greater resistance to softening than the composition designated

The qualities of balls incorporating 60 such compositions may be intensified at or adjacent to the surface of the external layer as for example by effecting local or uniform hardening by heat treatment with or without concurrent moulding 65 and/or vulcanisation, or by treatment of the surface with acids of the sulphonic group, especially sulphuric acid, or by

other chemical agents such as chlorine or formaldehyde.

Fibrous or other fillers such as wood flour may be incorporated in the composition to increase its toughness and suitable pigments such as titanium white to impart the desired colour and opacity.

Having now particularly described and

ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A process for the production of 80 games balls comprising forming the outer portion at least, of said balls of a non-aqueous mixture of gutta percha and a water resistant synthetic thermoplastic substance comprising a polymerisation 85 product of a member of the vinyl group or of a substitution derivative thereof.

2. A process according to the preceding

claim wherein said substance is incorporated with said gutta percha in the form 90 of polyvinyl acetate.

3. A process according to Claim 1 wherein said substance is incorporated with said gutta percha in the form of polyvinyl chloride.

4. A process according to Claim 1 when in said ambetance is incorporated

wherein said substance is incorporated with said gutta percha in the form of polyvinyl cyanide.

494,031

5. A process according to Claim 1 wherein said substance is incorporated with said gutta percha in the form of

polystyrene.

6. A process according to Claim I wherein said substitution derivative is incorporated with said gutta percha in the form of a polymerised vinylchlorethylene.

7. A process according to Claim 1. 10 wherein said substitution derivative is incorporated with said gutta percha in the with any of the preceding claims.

form of a polymerised methylvinyl. cyanide.

8. A process according to any one of 15 Claims 1 to 7 wherein said substance or

substitution product is incorporated with

substitution product is incorporated with said gutta percha in the proportion substantially of one part to three by weight.

9. A process for the production of golf and other balls for games as claimed in 20 any, of the preceding claims substantially as described with reference to the accompanying arguments.

panying examples.

10. Golf and other balls for games hav-

Dated the 21st day of March, 1938. W. BOND, Acting for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press .- 1938.

UK Patent Application (19) GB

(11) 2 245 580₍₁₉₎A

(43) Date of A publication 08.01.1992

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- (22) Date of filing 17.05.1991
- (30) Priority data (31) 908095
- (32) 01.05.1990
- (33) KR

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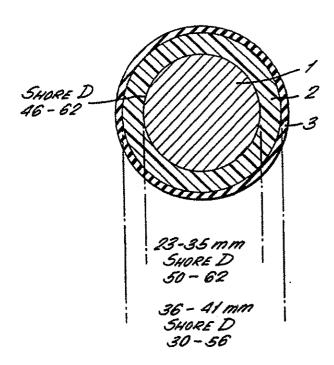
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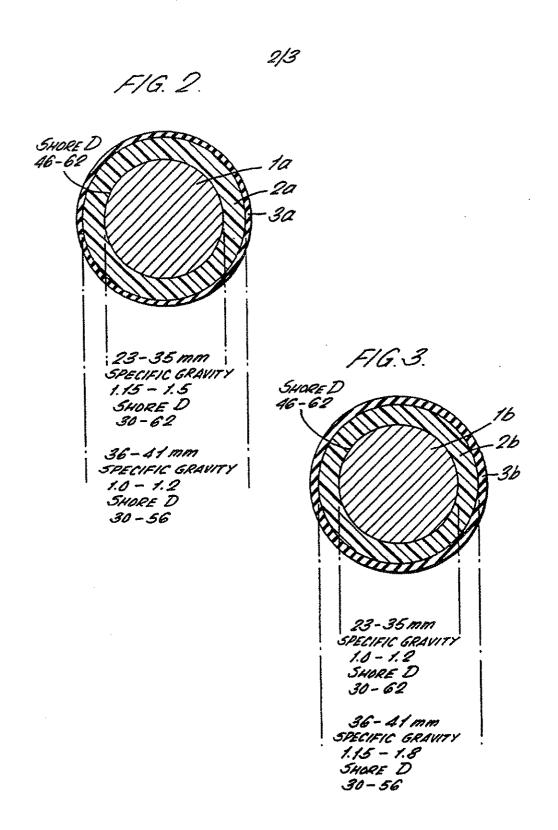
(54) Solid three-piece golf ball

(57) A non-wound three-piece golf ball comprises an inner core, an outer layer and a cover, the inner core having a diameter of 23 - 35 mm and hardness (Shore D) of 30 - 62, the outer layer having a diameter of 36 - 41 mm and a hardness (Shore D) of 30 - 56, the golf ball having a hardness (Shore D) 46 - 62 at the outer site in the inner core, which is located at the interface between the inner core and the outer layer of the golf ball and the hardness then decreases towards both sides.

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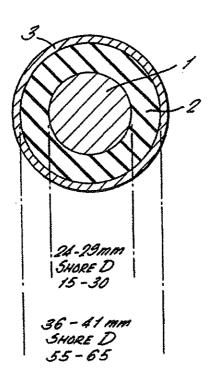
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SOLID THREE-PIECE GOLF BALL

The present invention relates to a solid three-piece golf ball having improved rebound characteristics and carry distance while maintaining adequate spin performance. These properties are obtainable by controlling the size of the inner core and outer layer as well as the specific gravity and hardness.

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The carry distance and spin performance of a golf ball are very important for the game. Although a solid two-piece ball generally has good rebound characteristics and carry distance, the core is too hard to provide a good spin performance. On the other hand, while a thread wound golf ball generally has a good spin performance, the rebound characteristics and carry distance deteriorate as the wound thread is loosened by prolonged use of the ball.

US patent No. 4,781,383 discloses a solid three-piece ball as shown in Fig. 4, which was obtained by controlling the size and hardness of the inner core and the outer layer. This ball has a carry distance similar to that achieved by a solid two-piece ball and feels similar to a conventional thread wound ball. However, this ball has a soft inner core and a hard outer layer. Therefore, it cannot provide a satisfactory carry distance and spin performance.

The total distance achieved by a golf ball includes the carry distance and the run distance. However, the carry distance is very important since the run distance is not accurate due to the unevenness

of the ground. The carry distance of a golf ball is directly influenced by its rebound characteristics. Under identical rebound characteristics and aerodynamic conditions (dimple characteristics of the ball), the lifting ability of a ball is improved if the spin rate is increased. Therefore, the peak of the trajectory gets higher, thereby providing an increase in carry distance, as the spin rate increases until the spin rate is increased up to about 2500 - 3000 RPM, when the ball is struck by a driver.

The present invention provides a solid three-piece golf ball having superior rebound characteristics and carry distance, while maintaining adequate spin rate. These effects are achieved by controlling the sizes, specific gravity and hardness of each part of the solid three-piece golf ball.

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In accordance with the present invention there is
provided a solid three-piece golf ball comprising a
core assembly provided by an inner core 1 and an outer
layer 2 and a cover 3 characterized by the following
features:

- 25 a) the inner core 1 has a diameter in the range 23 35 mm and hardness (Shore D) in the range 30 62;
- b) the outer layer 2 has a diameter in the range 36 41 mm and hardness (Shore D) in the range 30 56;
 - c) the golf ball has a maximum hardness (Shore D) in the range of 46 - 62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases

towards both sides.

Referring to the drawings:-

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5 Pig. 1 is a sectional view of a solid three-piece golf ball in accordance with the present invention.

Fig. 2 is a sectional view of a first embodiment (type 1) of the golf ball according to the present invention.

Fig. 3 is a sectional view of a second embodiment (type 2) of the golf ball according to the present invention.

Fig. 4 is a sectional view of the solid three-piece golf ball according to the USP 4,781,383.

As shown in Fig. 1, the solid three-piece ball according to the present invention comprises an inner core (1), an outer layer (2) covering the inner core and a cover (3) for protecting the outer layer.

If the surface of the inner core of the solid two-piece ball is soft, the difference between the moduli of elasticity of the inner core and the cover is increased. This generally tends to cause a reduction of rebound coefficient of the ball.

of a solid three-piece golf ball can be improved by controlling the hardness distribution in the outer layer and the inner core in such a way that the golf ball has a maximum hardness at the outer site in the inner core as shown in Fig. I, which is located at the interface between the inner core and the outer layer of the golf ball, and then the hardness decreases from that site both towards the outer surface of the outer layer and towards the center of the inner core. It has also been found that such a distribution of hardness in the core assembly allows a high energy to accumulate at the interface region where the hardness is maximum.

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Therefore, when the solid three-piece golf ball according to the present invention is struck by the club, the energy of the club face is efficiently delivered to the maximum hardness region and transferred toward the inner core without loss thus resulting in a high rebound coefficient. It has been observed that the fluctuation of hardness (Shore D) within 2, however, does not adversely affect the efficient transfer of the energy or spin performance of the golf ball of the present invention.

It has been found that the golf ball according to the present invention has adequate spin performance to provide an optimum trajectory resulting in an increase of carry distance since the outer layer is softer than the inner core. Furthermore, the golf ball of the present invention advantageously provides a delayed departure of the golf ball during the putting.

The diameter of the inner core of the golf ball according to

20 the present invention is set to 23 - 35 mm. If the diameter of the
inner core is less than 23 mm, the diameter of the soft outer layer has
to be increased and rebound characteristics are adversely affected. On
the other hand, if the diameter of the inner core exceeds 35 mm, the
diameter of the outer layer has to be decreased, and feeling would be

25 adversely affected due to the hard inner core.

The hardness (Shore D) of the inner core is preferably set in the range of 30 - 62. A inner core having a hardness (Shore D) less than 30 is too soft to give rebound characteristics necessary for reaching near the initial velocity limitation 250 ft/sec (+2 % tolerance) required by U.S.G.A. and R. & A. If the hardness (Shore D) exceeds 62, the feeling of the ball is adversely affected.

The diameter of the outer layer is set to 36 - 41 mm.

35 If it is less than 36 mm, the carry distance will be decreased due to the increased thickness of the cover.

On the other hand, if the diameter of the outer layer is

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greater than 41 mm, the thickness of the cover will have to be decreased thereby adversely affecting the durability of the ball.

The hardness (Shore D) of the outer layer is set to 30 - 56 since if the outer layer has a hardness (Shore D) less than 30 it is too soft to provide the rebound characteristics necessary for reaching near the initial velocity 250 ft/sec (+2 % tolerance). If the hardness 10 (Shore D) exceeds 56, it is difficult to obtain an adequate spin performance.

The hardness (Shore D) of the outer site in the inner core, which is located near the interface between the inner core and the 15 outer layer, is set to 46 - 62 because, if the hardness (Shore D) is less than 46, it is not possible to accumulate a high energy, while, if the hardness (Shore D) is greater than 62, the feeling of the ball will be adversely affected.

The first embodiment (type 1) shown in Fig. 2 of the present 20 invention has the following specification:

Inner core

Dismeter (mm): 13 - 35 25 Specific gravity: 1.15 - 1.5 Bardness (Shore D): 30 - 62

Outer layer

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Diameter (mm): 36 - 41 Specific gravity: 1.0 - 1.2 Hardness (Shore D): 30 - 56

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The outer site in the inner core

Hardness (Shore D): 46 - 62

The solid three-piece ball of this type provides a superior carry distance even if the cover (3a) is made of hard resin since the outer layer (2a) is soft and the specific gravity of the inner core is greater than that of the outer layer, which provides an adequate spin performance, when the ball is struck by club, allowing an optimum trajectory and a superior carry distance of the ball. This type of golf ball especially provides a keen back spin when the ball is struck by a short iron.

The second embodiment of the present invention as shown in Fig. 3 has the following specification.

Inner core

Diameter (mm): 23 - 35 Specific gravity: 1.0 - 1.2 Hardness (Shore D): 30 - 62

Outer layer

Diameter (mm): 36 - 41

Specific gravity: 1.15 - 1.8

Hardness (Shore D): 30 - 56

The outer site in the inner core

Hardness (Shore D): 46 - 62

Generally, the carry distance is decreased if the specific

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gravity of the outer layer is greater than that of the inner core. However, the solid three-piece ball having the above specification provides a superior carry distance since the outer layer (2b) is soft and an sadequate spin performance allows an optimum trajectory to be formed, although the cover (3b) is made of hard resin. This type of golf ball especially provides a trajectory which is less affected by the wind.

ts own characteristics, and a golfer may choose any type of golf ball depending on the peculiarity of his swing, such as, e.g., club head speed, ability of producing spin, and angle of launching the ball.

The inner core and the outer layer comprises a rubber base, co-cross linking agent, filler, polymerization initiator, antioxidant and the like. As a base rubber, Cis - 1, 4 polybutadiene alone may be used. If necessary, natural rubber, isoprene rubber, and/or styrene-butadiene rubber may be optionally added to 1, 4 - 20 polybutadiene.

The co-cross linking agent comprises a compound selected from Carbylenically unsaturated carboxylic acids and metal salts thereof. Trimethylol propane trimethacrylate may be optionally added.

Examples of Carbylenically unsaturated carboxylic acids are acrylic acid and methacrylic acid. Metal sats thereof include zinc diacrylate, zinc dimethacrylate, and the like.

The amount of co-cross linking agent used in the inner core is 35 - 50 parts (weight) for 100 parts (weight) of the base rubber, while the amount of co-cross linking agent used in the outer layer is 25 - 40 parts (weight).

Fillers which can be used include metal oxides, such as, lead oxide, iron oxide as well as barium sulfate, silica, calcium carbonate and the like. If acrylic acid or methacrylic acid is used, the preferred filler is zinc oxide. The amount of the filler is not limited although it usually depends on the specific gravity or hardness of the inner core or the outer layer to be prepared. The preferred amount of the filler is 1 - 50 parts (weight) and of the base rubber is 100 parts (weight).

The polymerization initiator includes an organic peroxide, such as, dicumyl peroxide, N-butyl-4, 4'-bis (t - butylperoxy) valerate, bis (t - butylperoxy isopropyl) benzene, 1-1'-bis (t - butylperoxy)-3, 3, 5 - trimethyl cyclohexane. The amount of the initiator is 0.2-3.0 parts (weight) of the base rubber is 100 (weight).

If necessary, a coagent such as N-N'-m'-phenelene dimaleimide and the like may be optionally used.

An antioxidizing agent, such as, 2-2'-methylene-bis

(4-methyl-6-t-butylphenol) and the like may be added. The amount is
preferably 0.5 - 1.5 parts (weight) of 100 parts (weight) of the base
rubber.

The process for preparing the inner core comprises
25 mixing the above components by a conventional mixing
apparatus, such as an internal mixer, two roll mill or
the like and then subjecting the composition to
compression or injection molding.

30 The compression or injection molding is an important step in the above process, in which the cross linking reaction by the co-cross linking agent takes place with the aid of the initiator under a given temperature and time so as to give the desired hardness distribution in 35 the inner core.

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The hardness distribution to be obtained is influenced by the co-cross linking agents and initiators as well as by the temperature and time used for curing.

For each co-cross linking agent, there is an initiator suitable for that co-cross linking agent. The amount of the cross linking agent may be minimized without adversely affecting the hardness distribution when the cross linking reaction is carried out at the reaction temperature, which is 10° - 50°C to higher than the decomposition temperature of the initiator used.

If the cross linking reaction takes place at a temperature lower than the above, the distribution of 15 hardness suitable for the present invention cannot be obtained, while, at a temperature higher than the above, a uniform distribution of hardness cannot be obtained.

If the cross linking agent is highly volatile, an 20 initiator with a relatively low decomposition temperature may preferably be used. While the co-cross linking agent is not highly volatile, an initiator having a higher decomposition temperature may preferably be used.

25 If the cross linking reaction takes place at a higher temperature, the rubber molecules are broken resulting in remarkable degradation of physical properties of the rubber, such as, the resilience and durability of the rubber, due to severe micro Brown 30 motion and nascent oxygen. Therefore, it is necessary to carry out the cross linking reaction with the aid of an initiator having a decomposition temperature which is 00 - 50°C lower than the boiling point of the co-cross linking agent, A. B. -ethylenically unsaturated carboxylic acid.

When an initiator having a relatively low decomposition temperature is used, it is necessary to carry out the cross linking reaction at the temperature which is 20° - 50°C higher than the decomposition temperature for a relatively long time, such as, 10 - 40 minutes so as to obtain an optimum hardness distribution without adversely affecting other physical properties.

On the other hand, if the initiator with a relatively high decomposition temperature is employed, it is necessary to carry out the cross linking reaction at a temperature which is 10° - 40°C higher than the decomposition temperature for a relatively short period of time, such as, 5 - 25 minutes.

According to the present invention, the cross 15 linking takes place and the curing of the rubber proceeds when the starting mixture is subjected to heat and pressure predetermined depending on the initiator used. When the heat is transferred through the mixture and rubber is expanded, the co-cross linking agent used is 20 partially evaporated near the metal oxides or salts and the co-cross linking agent in gaseous form migrates from the inner part of the inner core (1) towards the outer part of the inner core carrying out the cross linking reaction of the rubber with the aid of the initiator. 25 Therefore, the cross linking reaction is more active near the outer region of the inner core (1) than at the centre region of the inner core (1) thus resulting in a higher hardness near the outer surface than at the inner region of the core (1).

When the starting mixture is expanded by heating, the mold will be opened unless the mold is prevented from being opened by adding pressure.

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Acrylic acid or methacrylic acid form a high molecular weight polymer in the form of matrix having a metal nucleus. The uniformity of cis bonding or cross linking depends on the uniformity of the starting mixture and the heat transfer.

Even after the cross linking is completed, the mixture is continuously expanded by heat until the whole process is completed. It has been found that, due to the pressure added to prevent the opening of the mold, the most dense layers are formed in the region, which is near to the cavity of the mold, namely, the outmost region of the inner core, thus resulting in a gradual increase of the hardness from the centre of the inner core towards the outer part of the inner core forming a maximum hardness site near the interface.

The molecular chains in the most dense layers of the high molecular product are compressed like springs due to the pressure caused by the expansion of the mixture. Therefore, it is possible to store a higher energy.

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The outer layer (2) can be prepared by a process similar to that for the inner core (1), although the compression molding as described in the Example is preferred. However, it is important to prevent the outer surface of the outer layer from being too hard so as to obtain the desired hardness distribution as required in the present invention.

However, it is preferred that the crosslinking of the two-piece solid inner core assembly is carried out at a lower temperature than that for the crosslinking of the inner core to obtain the desired hardness distribution for the present invention.

The starting mixture for preparing the outer layer as well as the solid core is also expanded when it is subjected to heating. The expansion in the outer layer is greater than that in the inner core thus resulting in the most dense molecular chains being formed near the interface region between the inner surface of the outer layer and surface of the inner core.

Furthermore, a part of the cross linking agent included in the starting mixture for the outer layer evaporates and the gaseous components formed penetrate into the surface of the inner core rendering a strong binding of the outer layer with the inner core.

The resulting core assembly, which consists of the outer layer and the inner core, has such a hardness distribution that the peak of hardness appears at the outer site in the inner core, which is near the interface between the inner core and the outer layer and that the hardness is gradually decreased toward both sides.

When the ball is struck, it is presumed that the energy given by the club face is efficiently delivered and stored at the site where the hardness is the 10 highest. Then, the energy stored is released toward the inside of the inner core without loss thus resulting in a high rebound coefficient.

The core assembly has a diameter of 36 - 41 mm and a 15 hardness (Shore D) of 30 - 62. As mentioned earlier, two types of core assembly are available.

The core assembly is then covered with a resin having a good impact and weather resistance of 0.9 - 2.6 20 mm in thickness. The resin may contain inorganic filler, pigment and etc.

As a cover material, balata rubber or ionomer resin (such as "Surlyn" resin marketed by Du Pont Co.) or 25 polyurethane or the like is used, although the ionomer resins are preferred.

The covering is carried out by an injection or compression molding. Finally, the cover is painted to 30 obtain the solid three-piece ball according to the present invention.

As described above, according to the present invention, it is possible to obtain a solid three-piece 35 golf ball of the type (1) or (2) having excellent rebound characteristics and carry distance as well as a high spin performance by adjusting the size and specific

gravity as well as the hardness of each of the two pieces forming the core assembly.

The solid three-piece golf ball of the type (1) or (2) according to the present invention provides an excellent carry distance and a better control of the ball compared with a ball having a long roll distance since the golf ball according to the present invention will be least influenced by the ground condition of the field. The golf ball 10 according to the present invention also has an adequate spin performance.

Furthermore, it is possible to control the trajectory of the golf ball of type (1) or (2) using the different moment of inertia of each ball. Therefore, a golfer may select a suitable ball depending on his swing characteristics, such as, his club head speed, spinning ability and launching angle.

Example 1

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A starting mixture was prepared, which contained Cis - 1, 4 polybutadiene rubber (base rubber), zinc discrylate (co-cross linking agent), zinc oxide (filler), dicumyl peroxide (initiator), 2, 2' methylene - bis (4 - methyl - 6 - t - butyl phenol) (antioxidant) in the 25 amounts as indicated in the Table 1.

The mixture was mixed and kneaded by using a two roll mill for 30 minutes and pressure-molded at 165°C for 10 minutes to prepare a solid inner core.

The inner core was covered by hemispherical premold outer layers in a mold and the resultant product was cured by heating at 150°C for 20 minutes to obtain a two-piece solid core assembly. This core assembly was then covered by ionomer resin with same dimple design by an injection molding and then painted to provide a solid three-piece golf ball according to the present invention.

A solid two-piece golf ball was also prepared exactly in same way as the above.

5 24 of each type of golf ball were prepared which include the two types of solid three-piece golf ball (1, 2 in the Table 1) and the solid two-piece golf ball (3 in the Table 1). The golf balls were tested by a swing robot at a U.S. testing organization on the same day.

10 The results of the tests are tabulated in the Table 1.

The test club used was 9.5° Driver Steel S. Shaft made by Taylor Made Golf Co. and the head speed was 108 miles/hour. The trajectory was measured through a wire screen within one inch square increments. The range was 0 to 10. The number was recorded at the point which the ball reached its spex. These numbers are for reference only to other balls in the test.

Example 2

The starting mixture was prepared, which contained Cis - 1, 4 polybutadiene rubber (rubber), zinc diacrylate (co-cross linking agent), zinc oxide (filler), dicumyl peroxide, N - butyl - 4, 4' - bis (t - butylperoxy) valerate (initiator), 2, 2' - methylene - bis (4 - methyl - 6 - t - butyl phenol) (antioxidant) in the amounts as indicated in the Table 2.

Solid three-piece balls were prepared with the process of the Example 1.

The solid three-piece balls (two types) according to the present invention were prepared and tested (1 and 2 in Table 2).

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For comparison tests, three-piece solid golf balls commercially available (3 in Table 2) and thread wound balls (4 in Table 2) were also tested. 24 balls for each type of golf balls were used and tested

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under same method and conditions on the same day. The results of the tests are tabulated in Table 2.

From the Tables 1 and 2, it has been clearly proved that the solid three-piece golf ball according to the present invention has an excellent rebound characteristics, carry distance and an adequate spin performance.

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		Examp) e	Corparative Everple	
		1	٤		
	Composition of inner core (parts by weight)			Composition of corr (parts by veight)	
ļ	Cis-1.4 polybutediene rubber	100	100		100
	zinc discrylate	43	43		Ł0
	1	24.6	4.4		12.1
	zine oxide	3	3		3
	dicumyl peroxide(402)	0.5	0.5		0.5
	2,2'-methylene-bis(4-methyl -6-t-butyl phenol)				
ų,	Composition of out layer (parts by weight)				
mixture	3,000	100	100		
Ĭ.		35	3\$	****	
မ္မ	031 2 6	5.5	21.5		
Starting	SXCC .	3.	3		
Sta		0.5	0.5		
				Composition of cover	
	Composition of cover (parts by veight)			(parts by weight)	
	"Surly 8940" made by Du Pont	100	100	·	100
	Titanium dioxide	3.1	3.1		3 - 1
	Inner Core	•	•		
	Diameter(mm)	29.7	29.7		
	Weight (gr)	16.5	15	1	
	Specific gravity	1.20	1.09		
	Outer Core			Outer Core	
	Outer diameter (mm)	38.7	38.7		38-7
	Weight of core assembly(gr)	35.3	35.6		35.3
۷ ۵	Cover			Cover	
E	Diameter of fineshed ball(mm)	12.7	\$2.7		42.7
ŭ.	Reight of finished ball(gr)	45.3	45.5	•	45.3
cal Properties	Distribution of hordness	<u> </u>		Distribution of hardness	
Cal	(Shore D)	45	42	(Shore D)	38
-3	Center	ľ	. 50		Ā Ţ
Physi	Site 5mm apart from center	53 54	52		49
	Site 10mm apart from center	1	52 58		49
	Site 14mm apart from center	61	-		49
	Site 15mm apart from center	56	55		. 55
	Site 16mm aport from center	55	54 54		60
	Site 18mm sport from center	55	122		155
		126	243-23		239-1
į.	Carry distance(yds)	242.80	269.38		267.4
Character- iscies	Total distance(yds)	235.76	231.78		234.4
1351	Velocity(ft/sec)	1	5.52		5.2
5 🗂	Trajectory	5.54	3+76		

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r		Toble ? Examp	 le	Comparat	ive [xosp)c
l			2	3	<u> </u>
}			4	1	
	Corposition of inner core (parts by weight) Cis-1,4 polybutadiene rubber	100	100		
-	zinc diacrylate	38	ьo		
- 1	zinc oxide	34.2	6		
1	dicumy) peroxide(40%)	3	3		
	2,2'-methylene-bis(4-methyl -6-t-butyl phenol)	. 0.5	0.5		
mixture	Composition of out layer (parts by weight) Cis-1,4 polybutadiene rubber	100	100		
ž.	zinc diacrylate	32	29		
1	zinc oxide	3	24.4		
Starting	N-butyl-4,4'-bis(t- butylperoxy)valerate(402)	3.5	3.5		
St	2,2'-methylene-bis(4-methyl -6-t-butyl phenol)	0.5	0.5		
	Composition of cover (parts by weight) "Surly 8940" made by Du Pont	100	100		
	Titanium dioxide	3.1	3.1		_ ;
	Inner Core			•	
	Diameter(mm)	29.7	29.7		
	Weight (gr)	17-1	15.2		
	Specific gravity	1.25	1.11		
	Outer Core			Outer	Core
	Outer diameter (mm)	38-7	38.7	38.3	
	Weight of core assembly (gr)	35-3	35.4	34.7	
				Cove	: [
	Cover Diameter of finished ball(mm)	42.7	12 T	12.8	42.7
	Weight of finished ball(gr)	45.3	45.3	45.0	45.5
ea.	Distribution of hardness				
ä	(Shore D) Center	38	39	1	
d o	Site Sam apart from center	ls.	46		
gi.	Site 10mm apart from center	45	47		
101	Site 14mm apart from center	52	53		
Physical Properties	Site 15mm spart from center	15	39	1	
	Site 16mm spart from center	. 44	38		
	Site 18mm apart from center	b b	38		
		108	108	155	90
	Carry distance (yds)	223.12	223 - 67	213.20	221 - 79
1	Total distance(yds)	253.04	256.12	248.00	251-83
5	· · · · · · · · · · · · · · · · · · ·		235.46	233.41	231 - 23
Character- iscies	Velocity((t/sec)	235.67	233.40		\$-12

CLAIMS:

- 1. A solid three-piece golf ball comprising a core assembly provided by an inner core 1 and an outer layer 2 and a cover 3 characterized by the following features:
- a) the inner core 1 has a diameter in the range
 23 35 mm and hardness (Shore D) in the range10 30 62;
 - b) the outer layer 2 has a diameter in the range 36 - 41 mm and hardness (Shore D) in the range 30 - 56;
- c) the golf ball has a maximum hardness (Shore D) in the range of 46 62 at the outer site of the inner core which is located at the interface between the inner core 1 and the outer layer 2 of the golf ball and the hardness then decreases towards both sides.
- A solid three-piece golf ball according to claim
 in which the specific gravities of the inner core 1
 and the outer layer 2 are in the ranges 1.15 1.50
 and 1.00 1.20, respectively.
- A solid three-piece golf ball according to claim
 in which the specific gravities of the inner core 1
 and the outer layer 2 are in the ranges 1.00 1.20
 and 1.15 1.80, respectively.
- 4. A solid three-piece golf ball according to any one of claims 1 3, in which the site of maximum
 35 hardness is located 11.5 17.5 mm from the centre of the ball.

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5. A solid three-piece ball according to any one of claims 1 - 4, in which the minimum hardness (Shore D) difference between the said outer site in the inner core 1 and the inner site in the outer layer 2 of the ball is 3.

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- (33) FR
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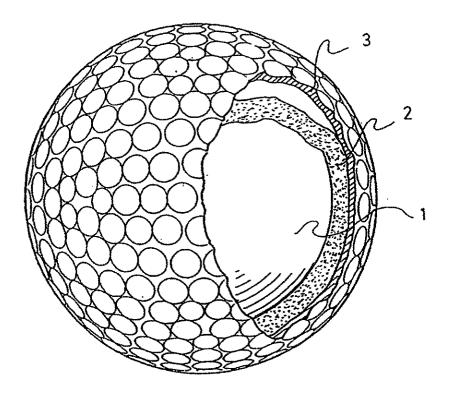
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- (56) Documents cited GB 2086235 B
- (58) Field of search UK CL (Edition K) A6D D1A D1B D1C1, C3V VEM INT CL A63B W.P.I.; CLAIMS

(54) Golf balls of three piece structure

⁽⁵⁷⁾ A golf ball comprises a three part structure, namely an elastometic core, an intermediate layer, and a thermoplastic outer envelope. The intermediate layer is made of a thermoplastic material containing at least 10% and preferably at least 35% by weight of a block copolyether.

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FIGURE DE L'ABREGE



- 1 -

GOLF BALL

This invention relates to golf balls and, more particularly, to golf balls having a three piece structure.

The prior art makes a distinction between two main types of golf ball. One of these is the solid so-called "two-piece" ball. Its properties result from the combination of a one-piece rubber spherical core and a hard thermoplastics envelope of ionomer resin. The main advantage of these balls is that they give very high performance in long drives because of their high starting speed. On the other hand they feel hard when hit, the essential cause of which is their significant rigidity. In short shots or approach shots, their high initial speed and the low contact area with the striking face reduces control of the ball and the lack of rotational speed has an adverse effect on the behaviour of the ball as it drops.

The other main type of golf ball is the socalled "three-piece" ball. These comprise a central solid or liquid core, a winding of rubber threads forming an intermediate layer, and a thermoplastics outer envelope, one or two millimeters thick, of ionomer resin or balata rubber. The greater deformability of the outer layers of this structure causes a feeling of softness on impact, due to the greater level of compression, and there is also a larger contact area. Conversely this type of ball has a poorer performance in long shots, the opposite of "two piece" balls.

An object of this invention is to provide a golf ball having a structure such that its performance is satisfactory in all parts of the game, namely: an initially high speed, close to that of two piece balls, good feel and good control in the approach game, and also reproducibility of strike and excellent durability.

According to the present invention there is provided a golf ball which comprises a core of elastomeric material, an intermediate layer, and an outer envelope of thermoplastic material, in which the intermediate layer is made of a composition containing at least 10% by weight of a block copolyether, based on the total weight of the composition.

The intermediate layer preferably comprises at least 35% by weight of the block copolyether.

The block copolyethers used in the intermediate layer according to the invention are a known class of block copolymers comprising polyether blocks of a certain chain length and blocks derived from the other monomer or monomers. In the block copolymers used according to the present invention, the polyether blocks are flexible and the other blocks should be rigid. By varying the nature and proportions of these components a fairly wide range of products can be obtained, from the very flexible to the relatively rigid.

Of these copolymers, those which are particularly preferred are amide block copolyethers and ester block copolyethers. Suitable amide block copolymers (PEBA) are, for example, those available under the trade mark "Pebax" from Atochem; under the

trade mark "Grilamid" from EMS; and under the trade mark "Vestamid" from Huls.

Preferred ester block polyethers (PEBE) are those in which the ester blocks are derived from butylene terephthalate (PBT). Suitable block copolymers of this kind are, for example, those available under the trade mark "Hytrel" from du Pont and under the trade mark "Arnitel" from Akzo.

The intermediate layer may be formed wholly of the block copolyether. The resulting balls are valued for their excellent touch and their high initial speed. Conversely, because of a low elastic modulus they have a tendency to deform excessively on impact.

This problem is advantageously solved by using a mixture of the ether block copolymer and one or more ionomers. The proportion of ionomer(s) may be up to 90% by weight of the composition and is preferably from 20 to 65% by weight. Preferred ionomers are those having a Shore D hardness of from 55 to 65 and a bending modulus of from 250 to 350 N/mm2. In this case, the block copolymer is preferably an amide block polyether and is present in a proportion of from 35 to 80%; the amide block polyether is preferably one having a Shore D hardness of from 30 to 40.

For the better understanding of the invention, preferred embodiments thereof will now be described, by way of example, with reference to the accompanying drawing, in which the single figure is an elevation of a golf ball according to the invention, in partial cross-section.

Referring to the figure, the golf ball comprises a core 1 formed of a thermoplastic, thermo-hardened or vulcanisable elastomer and having a diameter of from 34 to 38 millimetres. Its density is from 1 to 1.3 g/cm3 and its Shore D hardness is from 40 to 50.

The compression of the core under a load of 150 kg is from approximately 2.8 to 4.5 mm for a fixed diameter of 36 mm.

Preferred elastomers for the core are crosslinked diene elastomers of the cis-1,4-polybutadiene type containing a reaction product based on zinc oxide and zinc diacrylate. The core composition also contains a cross-linking agent, for example dicumyl peroxide.

The intermediate layer 2 is an injectable and extrudable thermoplastic amide block polyether copolymer and, preferably, a polyetheresteramide of the kind described in French Patent 2,273,021.

By way of example, balls have been made with an intermediate layer of "Pebax" alone. Their characteristics and properties are shown in Table I and II below.

In a preferred embodiment, the intermediate layer 2 is formed of a mixture of amide block polyether and ionomer(s). Tables 3 and 4 show the characteristics and properties of balls having intermediate layers formed of mixtures of "Pebax" 3533 and "Escor".

In general, the layer 2 has a thickness of approximately 1 to 3 mm and an elastic modulus of from 15 to 255 N/mm2. Depending on the type of copolymer used, the Shore D hardness may vary from 25 to 50. The effect of these parameters is important and governs the performance characteristics of the ball. Balls having an intermediate layer with a low Shore D hardness of about 30 to 37 (low bending modulus) are valued for their touch and their control because of their high rotational speed or spin. Conversely, balls in which the Shore D hardness of the intermediate layer is from 40 to 50 (bending modulus also higher) are valued for

their optimum initial speed and their durability.

If Tables I and III are compared, it will be noted that the hardness values do not change if an ionomer is added to the ether block copolymer.

Conversely, the modulus of elasticity under tension increases considerably. This effect is particularly useful because the intermediate layer contributes to the mechanical strength of the core on impact and advantageously restricts its deformation. The intermediate layer behaves dynamically like the wound elastic filament layer of so-called "wound" balls.

The assembly of the two parts 1 and 2 forming the internal structure of the ball has a compression under 150 kg of 2.5 to 4 mm for a total diameter of 40 mm.

Outer layer 3 forms the envelope for the ball. It is made of a thermoplastics material and has a thickness of from 0.9 to 3 mm.

The choice of materials is relatively wide in so far as the essential qualities required of the envelope are its impact resistance and durability. To obtain these characteristics, it is generally required that the hardness of the envelope should be greater than the hardness of the intermediate layer.

Suitable Shore D hardnesses for the envelope are, for example, from 40 to 55 and preferably from 43 to 48; the density of the envelope is preferably from 0.8 to 1.2 g/cm3 and the bending modulus is preferably from 30 to 280 N/mm3.

Preferred envelope materials are "Surlyn" ionomers available from du Pont and "Iotek" ionomers available from Exxon; amide block copolymers of the same type as those used for the intermediate layer, but of greater hardness; mixtures of ionomers and amide block copolymers; thermoplastic polyurethanes; and

mixtures of two or more of these materials.

The combination of the three components 1, 2 and 3 gives rise to a finished ball having a diameter of from 42.7 to 42.8 mm. Its compression under a load of 150 kg is from 2.5 to 4 mm.

By way of example, the physical and behavioural characteristics and properties of several balls according to this invention have been compared with balls according to the prior art in common commercial use. The results are shown in Tables I to IV below:

									7 -					······································
	Ball B				MOTIND CORE						BALATA	ENVELOPE		
PRIOR ART	3- Piece	4				WOUND CORR					SURLYN	ENVELOPE		
I 33	2-Piece Ball		SOLID RUBBER CORE			and the second s					NA TOTA	ENVELOPE		
TABLE	Ball 04		36.4	.18		3.8	(PEBAX) R	43	1.01	80		22	1.35	120
	10N 101 03 B	CIS-1,4-POLYBUTADINE ELASTOMER CORE	36.4	1.18		3.8	AMIDE BLOCK COPOLYETHER (PEBAX INTERMEDIATE LAYER	40	3.0.	វេ		C ENVELOPE	1.35 1.35	100
	INVENTION	-1,4-POLYE	36.4	1.18		3.8	OCK COPO NTERMEDI	37	1.01	40	2	THERMOPLASTI	1, 345 2, 1, 3, 45 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	100
	1 10 11-0	l l	36.4	1.18		3.8	AMIDE BL	37	8.1.	(Ç.	THER	2 E. C.	80
	ļ	COMPOSITION	Diameter (mm)	Density (g/cm3)	Compression in mm under a	constant load of 150 Kg	COMPOSITION	Hardness (Shore D)	Thickness (mm) Density (g/cm3)	Elastic Modulus (N/mm2)	under tension	COMPOSITION	Hardness (Shore D) Thickness (mm) Density (g/cm3) Elastic modulus	

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				TABLE	II		
		INVENTION				PRIOR ART	Вэ
	Ball 01	Ball 02	03	Ball 04	2-Piece Ball	A A	8
O to	42.7	42.7	42.7	42.7	42.7	42.7	42.7
מושפרפי וווווו		A. A.	A 2.	45.4	. 45.5	45.4	45.3
Weight (g)		r 				~	3.2
Compression (mm)	3.7	3.6	3.4	3.1	2.8	5.5	
DRIVER							
Initial speed (m/s)	64.2	40	64.2	64.4	64.7	64.3	64.2
apeada		1	000	0000	. 0000	3300	3700
Spin (rpm)	3800	3650	3600	3300	227		
5 IRON							Ç
Spin (rpm)	7500	7300	7300	6800	2600	0059	0367
PROPERTIES							
Control	<u>ن</u>	U	<u>6</u>	EJ.	Σ	Ö	(±)
; ; ; ; ; ; ; ; ; ; ; ;	<u></u>	ט	M	v	Σ	U	(L)
Durahilito	U	ტ	O	U	M	O	Σ
Reproducability		Ed	ω	EŽ	v	æ	Σ
E=Excellent	gg =	M=Mediocre	locre				

	Ball 07	ELASTOMER CORE	36.4 1.18	3.8	V/IONOMER)	43	150	340	1.35	120
	Ball 06		36.4 1.18	3.8	INTERMEDIATE LAYER (PEBA/IONOMER)	1,8	120	THERMOPLASTIC ENVELOPE	1,35	100
TABLE III	Ball 05	CIS-1,4-POLYBUTADIENE	36.4	3.8	INTERMED	3.1	06	THE	1,35	06
		NOTETECOMO	Diameter (mm)	Compression in mm under 150kg	WOLET SOCIETY	Hardness (Shore D) Thickness (mm) Density (q/cm3)	Elastic Modulus (N/mm2) under tension	COMBOSTITION	Hardness (Shore D) Thickness (mm) Density (g/cm3)	Elastic Modulus (N/mm2) under tension

	u	

	TABLE IV		
	Ball 05	Ball 06	Ball 07
			1
Diameter (mm)	42.7	42.7	47.
Weight (g)	45.4	45.4	45.4
DRIVER (46 m/s)			
Initial speed (m/s)	64.2	64.3	64.2
Spin (rom)	3800	3600	3400
5 IRON			
Spin (rpm)	7500	7300	0069
PROPERTIES:			
Control	េ	ъ	U
6	Ø	ដ	v
Durability	U	O	υ
Reproducability	li li	ω	មា
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Claims:

- 1. A golf ball which comprises a core of elastomeric material, an intermediate layer, and an outer envelope of thermoplastic material, in which the intermediate layer is made of a composition containing at least 10% by weight of a block copolyether, based on the total weight of the composition.
- 2. A golf ball according to claim 1, in which the intermediate layer composition comprises at least 35% by weight of the block copolyether.
- 3. A golf ball according to claim 1 or 2, in which the block copolyether is an amide block copolyether.
- 4. A golf ball according to claim 3, in which the amide block copolyether is a polyetheresteramide.
- 5. A golf ball according to any of claims 1 to 4, in which the intermediate layer composition consists of a mixture of the block copolyether and at least one ionomer.
- 6. A golf ball according to claim 5, in which the composition contains up to 90% by weight of one or more ionomers having a Shore D hardness of from 55 to 65 and a bending modulus of from 250 to 350 N/mm².
- 7. A golf ball according to claim 6, in which the composition contains from 20 to 65% by weight of said ionomer(s).

- 8. A golf ball according to claim 7, in which the intermediate layer composition contains 35 to 80% by weight of an amide block polyether having a Shore D hardness of from 30 to 40.
- 9. A golf ball according to any of claims 1 to 6, having the following physical and dimensional characteristics:

diameter of core- 34-38 mm diameter of core + intermediate layer- 37-41 mm diameter of whole ball-42.7-42.8 mm thickness of intermediate layer-1-3 mm thickness of envelope-0.9-3 mm compression of core having a 36 mm diameter under a load of 150kg-2.8-4.5 mm compression of core + intermediate layer having a 40 mm diameter under a load of 150 kg-2.5-4.0 mm compression of whole ball under a load of 150 kg-2.5-4.0 mm elastic modulus (ASTM) of intermediate layer-15-250 N/mm² elastic modulus (ASTM) of envelope-30-280 N/mm²-

- 10. A golf ball according to any of claims 1 to 9, in which the core comprises a cross-linked elastomer of the diene type.
- 11. A golf ball according to claim 10, in which the elastomer is based on cis-1,4-polybutadiene.

- 12. A golf ball according to any of claims 1 to 11, in which the Shore D hardness of the core is from 40 to 50.
- 13. A golf ball according to any of claims 1 to 12, in which the hardness of the envelope is greater than that of the intermediate layer.
- 14. A golf ball according to claim 13, in which the Shore D hardness of the intermediate layer is from 25 to 50.
- 15. A gold ball according to claim 13 or 14, in which the Shore D hardness of the envelope is from 40 to 55.
- 16. A golf ball according to claim 15, in which the Shore D hardness of the envelope is from 43 to 48.
- 17. A gold ball according to any of claims 1 to 16, in which the envelope is made of an ionomer, an amide block copolyether, a mixture of an ionomer and an amide block copolyether, a thermoplastic polyurethane, or a mixture of two or more of these materials.
- 18. A golf ball substantially as herein described with reference to any of Balls 01-07 of the Examples.

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(54) Golf ball

(57) A golf ball is provided having a core and a cover wherein the cover comprises a blend of low flexural modulus ionomer resins. Surprisingly, such blends exhibit spin properties, coefficient of restitution, initial velocities and cut and abrasion resistance comparable to or better than golf balls of the prior art. In each case the resins have a flexural modulus of 2000 -15000 p.s.i. and the cover has a Shore D hardness of 35 - 55.

GOLF BALL

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This invention relates to a golf ball having an improved cover composition which imparts to the ball superior playing properties and superior cut and abrasion resistance.

provided with covers made of balata or balata blends. Such balata covers were readily adaptable to the molding techniques commonly used in golf ball manufacture. Balata covered balls were also preferred by relatively skilled players because the relative softness of the cover material allowed the player to apply a spin to the ball to control the ball in flight and on the green. Such balata covered balls were disadvantageous, however, in that they had low tear resistance and were easily cut in play. Balata covered balls therefore had a relatively short life span.

been manufactured of a family of ionomers sold by E.I. duPont de Nemours & Company under the trademark SURLYN. These ionomers are described in U.S. Patent No. 3,264,272, issued August 2, 1966 to Rees, assigned to duPont and entitled "Ionic Hydrocarbon Polymers," the disclosure of which is incorporated herein by reference.

Golf balls having covers of various ionomers and ionomer blends have been disclosed in the prior art:

U.S. Patent No. 3,454,280, issued July 8, 1969 to Harrison, discloses golf balls having covers comprising a copolymer of ethylene and an unsaturated monocarboxylic acid, where the copolymer may be a terpolymer of ethylene, an unsaturated monocarboxylic acid, and a metal salt of an

unsaturated monocarboxylic acid. The golf balls have improved cutting resistance relative to balata covered balls.

U.S. Patent No. 3,819,768, issued June 25, 1974 to Molitor, discloses golf balls having covers comprising mixtures of sodium and zinc salts of ionic copolymers of olefins and unsaturated monocarboxylic acids.

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U.S. Patent No. 4,323,247, issued April 6, 1982 to Keches, discloses golf balls having covers composed of at least three ionomeric resins wherein one of the resins is a copolymer of ethylene and a sodium salt of methacrylic acid and the other two are copolymers of ethylene and a zinc salt of methacrylic acid, each of the three ionomeric resins having specifically defined amounts of free acid and metal ion.

U.S. Patent No. 4,337,947, issued July 6, 1982 to Saito et al., discloses a golf ball having a cover comprising an ionomer which is a copolymer of an olefin and a salt of an unsaturated carboxylic acid, and a polyester elastomer.

U.S. Patent No. 4,884,814, issued December 5, 1989 to Sullivan, discloses a golf ball having a cover comprising a blend of a hard ionomer resin and a soft ionomer resin.

U.S. Patent No. 4,911,451, issued March 27, 1990 to Sullivan et al., discloses a golf ball having a cover comprising blends of zinc or sodium neutralized ethylene-acrylic acid copolymers.

The golf balls of the prior art as disclosed in the aforementioned U.S. patents have varying properties with regard to playability, cut resistance, coefficient of restitution, and initial velocity.

It is an object of the invention to provide a golf ball having an improved cover composition which imparts the playability characteristics desired by the skilled player, while at the same time providing excellent cut resistance, abrasion resistance, coefficient of restitution, and initial velocity.

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In accordance with the invention, a novel golf ball is provided having a unique cover composition which imparts improved properties to the golf ball. Applicant has discovered that, unexpectedly, golf ball covers can be made of blends of only low modulus ionomeric resins, which blends have hardness values comparable to those of Balata covers while exhibiting cut resistance and playing life comparable to prior art golf balls having covers of blends having higher hardness values and including higher modulus ionomeric resins.

Each of the low modulus ionomeric resins used in the improved cover of the inventive golf balls has a flexural modulus value of about 2000 psi to about 15,000 psi. The covers of golf balls of the instant invention have a Shore D hardness value in the range of about 35 to about 55. This compares favorably with Balata covers, which typically have a Shore D hardness of about 43. It has been found that golf balls made in accordance with the instant invention have excellent playability characteristics, coefficients of restitution, and initial velocity values.

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Golf balls made in accordance with the instant invention comprise a core and a cover, wherein the cover is made of an improved composition comprising two or more ionomer resins having relatively low flexural modulus values and excluding ionomer resins having relatively high flexural modulus values. The resins of the cover composition are selected and combined in pre-determined proportions such that the Shore D value of the cover composition is in the range of about 35-55.

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modulus resin is one which has a flexural modulus value of about 2,000-15,000 psi when measured in accordance with ASTM method D-790. Thus, the low modulus resins used in the golf balls of the instant invention are distinguished from the high modulus resins used in prior art golf balls and which generally have flexural modulus values in the range of about 30,000-55,000 psi. Similarly, a low modulus resin will typically have a Shore D hardness value in the range of about 20-55 when measured in accordance with ASTM method D-2240. These low modulus resins are distinguished from high modulus resins used in prior art golf balls which have Shore D hardness values of about 60 and above.

Among the low modulus ionomer resins that may be used in the golf ball of the instant invention are some of the low modulus resins sold by the E.I. duPont de Nemours & Co. under the trademark Surlyn. Such low modulus ionomer resins may be a sodium or zinc salt of a terpolymer of an olefin having from 2 to 8 carbon atoms, an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms and an unsaturated monomer of the acrylate ester class having from 2 to 22 carbon atoms.

Typically, the olefin may be ethylene, the unsaturated monocarboxylic acid may be methacrylic acid, and the unsaturated monomer of the acrylate ester class may be iso-butyl acrylate or n-butyl acrylate. Exemplary of such resins are those disclosed in U.S. Patent No. 4,690,981, issued september 1, 1987 to Statz, the disclosure of which is incorporated herein by reference in its entirety.

Examples of low modulus ionomer resins suitable for use in the inventive golf balls with improved covers include the following:

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	Surlyn AD-8265	:	73% ethylene 17% n-butyl acrylate 10% methacrylic acid (sodium salt)
5	Surlyn AD-8269	:	68% ethylene 23% n-butyl acrylate 9% methacrylic acid (sodium salt)
	Surlyn 9020	:	80% ethylene 10% iso-butyl acrylate 10% methacrylic acid (zinc salt)

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These resins have the following properties:

		Flexural Modulus (psil	Shore D <u>Hardness</u>
15 .	Surlyn AD-8265	7,100	39
	Surlyn AD-8269	2,800	25
	Suryln 9020	14,000	55

In accordance with the invention, low modulus ionomer resins such as those identified above can be selected and blended in pre-determined proportions to produce golf ball cover compositions having the desired flexural modulus and Shore D hardness values.

It has been found that, unexpectedly, such golf balls exhibit excellent coefficient of restitution (COR) values. COR is an indication of the distance a golf ball will travel when struck by a golf club. COR is determined by propelling a finished golf ball against a hard surface, and measuring both the initial and the rebound velocity. The COR is the ratio of the rebound velocity over the initial velocity. The inventive golf balls also exhibit excellent initial velocity when struck with a golf club moving at 90 m.p.h. at the point of impact.

Examples of golf balls having covers made of blends of low modulus ionomer resins in accordance with the instant invention are set forth in Table I below. As also shown in Table I, these golf balls have excellent coefficient of restitution and initial velocity values, which those skilled in the art will recognize as comparable to those of other competitive golf balls.

-6-

TABLE I

BLENDS		MEAN SHORE D HARDNESS(a)	HEAN FLEXURAL MODULUS (*)	COEFFICIENT OF RESTITUTION(b)	INITIAL VELOCITY, 90 HPH CLUB HEAD SPEED(b)
Example 1					
Component Part	e by Weight				
SURLYN 9020	80	49	11.760 рві	0.638	215.7 ft/sec.
SURLYH AD-8269	20				•
TITANIUH DIOXIDE	1.0				
ULTRAHARINE BLUE	0.01				
Example 2					
		47	10,810 psi	0.633	214.8 ft/sec.
SURLYN 9020	60 .	4.7	TO LOTO Por	***	
SURLYN AD-8265	30 10				
SURLYN AD-8269	1.0				
TITANIUM DIOXIDE	0.01				
ULTRAHARINE BLUE	0.01				
Example 3					
	50	47	10,550 psl	0.635	215.1 ft/eec.
SURLYR 9020	50	•••			
SURLYN AD-0265 TITANIUH DIOXIDE	1.0				
ULTRAHARINE BLUE	0.01				
DETERMENT BLUE	0.01				
Example 4					
SURLIN POZO	33	35	5,496 psi	0.619	210.5 ft/sec.
SURLYN AD-8269	67				
TITANIUM DIOXIDE	1.0				
OLTRAHARINE DLUE	0.01				
Example 5	;				
SURLYN 9020	60	43	9,520 psl	0.628	213.D ft/sec.
SURLIN AD-8269	40				
TITANIUH DIOXIDE	1.0				
ULTRAKARINE BLUE	0.01				
ODITORNINATIO DADO					

⁽a) Celculated as the arithmetic mean based on the proportions of each Surlyn resin and neglecting the effects of titanium dioxide and ultramarine blue.

⁽b) Average of test measurements made on 12 balls for each example blend.

In addition to the foregoing properties, tests were conducted wherein golf balls of the instant invention and of the prior art were subjected to repeated impacts using a square groove pitching wedge golf club. In these tests, three blends were prepared as follows:

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10	Blend A:	Surlyn 8940 Surlyn 8269 Titanium Dioxide Ultramarine Blue Mean Shore D hardness Mean flexural modulus	55 parts 45 parts 1 part 0.01 part 47. 29,310 psi
15	Blend B:	surlyn 9910 Surlyn 8940 Titanium Dioxide Ultramarine Blue Mean Shore D hardness Mean flexural modulus	50 parts 50 parts 1 part 0.01 part 65.5 49,500 psi
20	Blend C:	Surlyn 9020 Surlyn 8269 Titanium Dioxide Ultramarine Blue Mean Shore D hardness Mean flexural modulus	70 parts 30 parts 1 part 0.01 part 46 10,640 psi

For each of these blends, the Shore D hardness value and the flexural modulus values were calculated in the same manner as was used for Examples 1-5 in Table 1 above. Blend A is a typical blend of a high modulus resin and a low modulus resin such as those blends disclosed in prior art patent U.S.

4,884,814; Blend B is a typical prior art blend of only high modulus resins; and Blend C is a blend of only low modulus resins in accordance with the instant invention. It may be seen that Blend C of the instant invention has a Shore D hardness value very similar to prior art Blend A, but a much lower flexural modulus value.

The blends were tested by preparing three sets of six golf balls per set, each set of golf balls having covers prepared of one of the three blends, for a total of 18 balls. Each golf ball was struck six times in the exact same spot at

about 20 second intervals using a 50° loft, investment cast, square groove pitching wedge. A square groove wedge was selected for this test because the sharp edges of the square grooves are known to severely scrape and lacerate the surface of the golf ball, such that serious damage would be expected.

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The abrasion and cut resistance of the cover compositions were evaluated on a scale of 1-3, where 1 represents noticeable shredding of the cover and severe surface roughness due to abrasion; 2 represents small pieces cut from the ball, particularly at the edges of the dimples, plus noticeable abrasion; and 3 represents no shredding and only minor abrasion. The results within each set showed great consistency, and are set forth in Table II below.

TABLE II

	Blend	Abrasion and <u>Cut Resistance</u>
20	A B C	2 1 3

From these results, it may be seen that the balls of the instant invention having covers made of low modulus, lower hardness Blend C show significantly greater resistance to cutting and abrasion under severe test conditions than either of the higher modulus Blends A or B.

Another property of golf balls which is highly valued by skilled players is a high spin rate, which allows the skilled player to better control the placement of the ball on the green. To evaluate the spin rate of golf balls of the instant invention, three sets of golf balls of 24 balls per set were prepared, each set of balls having covers of Blends A, B, and C as described above, respectively, for a total of 72 balls. Each ball was struck with a 50° pitching wedge swung at 75 m.p.h. and the spin rate was measured by standard

techniques. The average spin rates for the balls of each of the three blends are as follows:

TABLE III

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<u>Blend</u>	Average Spin Rate (r.p.m.)
	9320
A	8520
В	9515
С	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,

Thus, it may be seen that the low modulus cover composition of Blend C advantageously gives the golf balls of the instant invention a spin rate significantly higher than either of the prior art golf balls having higher modulus covers.

tested for their initial velocity, carry distance (the distance the ball travels between the tee and the place at which it first lands on the ground), and the carry and run distance (the carry distance plus the further distance the ball bounces or rolls before coming to a stop). To evaluate these properties for golf balls of the instant invention, three sets of 24 balls each having covers of Blends A, B, and C, respectively, were prepared, for a total of 72 balls, as described above for the spin rate tests. Each ball was struck with a 11° driver swung at 95 m.p.h. The results are set forth in Table IV below.

TABLE IV

30	Blend	Average Initial <u>Velocity (ft./sec.)</u>	WASTOR	Average Carry and Run <u>Distance (ft.)</u>
	A B	215.5 217.7 215.8	229 232 231	247 251 248

This data indicates that golf balls of the instant invention having cover compositions of low modulus Blend C have performance values comparable to those of prior art golf balls having cover compositions of high modulus Blends A and B.

Those skilled in the art will recognize that certain compatible materials can be added to the cover compositions of the golf balls of the instant invention without adversely affecting the improved properties of those compositions. The compatible materials may include coloring agents, such as dyes and pigments, fillers, antioxidants, antistatic agents, and stabilizers. These additives generally comprise no more than about 5% by weight of the cover composition, and typically are on the order of about 1-2% or less by weight of the cover composition.

The golf balls of the instant invention are preferably made by injection molding the cover composition about golf ball cores. The golf ball cores may be of either the solid type or the wound type, as is known in the art. Techniques for injection molding resin cover compositions about golf ball cores are also well known to those skilled in the art of golf ball manufacture.

The foregoing detailed description of the invention is not intended to limit the scope of the invention. Other embodiments and modifications, which do not consistitute departures from the spirit of the invention, will be readily appreciated by those skilled in the art from the foregoing specification.

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CLAIMS:

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- 1. A golf ball having a core and a cover, said cover comprising a blend of two or more ionomer resins, wherein each ionomer resin present in said blend has a flexural modulus value of about 2000 psi to about 15,000 psi, said cover having a Shore D hardness value in the range of about 35 to about 55.
- 2. The golf ball of claim 1 wherein each said ionomer resin is a metal salt of a terpolymer of an olefin having from 2 to 8 carbon atoms, an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms, and an unsaturated monomer of the acrylate ester class having from 2 to 22 carbon atoms.
 - J. The golf ball of claim 2 wherein said olefin is ethylene.
 - 4. The golf ball of claim 2 wherein said unsaturated monocarboxylic acid is methacrylic acid.
 - 5. The golf ball of claim 2 wherein said unsaturated monomer of the acrylate ester class is selected from the group consisting of n-butyl acrylate and iso-butyl acrylate.
 - The golf ball of claim 2 wherein said metal is selected from the group consisting of sodium and zinc.
 - 7. The golf ball of claim 1 wherein said cover comprises (a) a zinc salt of a terpolymer of ethylene, methacrylic acid, and iso-butyl acrylate, and (b) a sodium salt of a terpolymer of ethylene, methacrylic acid, and n-butyl acrylate.

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8. The golf ball of claim 7 wherein said cover further comprises (c) a second sodium salt of a terpolymer of ethylene, methacrylic acid, and n-butyl acrylate.

9. A golf ball as claimed in claim 1 substantially as hereinbefore described.

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Patents Act 1977 xaminer's report to the Comptroller under Section 17 (The Search Report)

Application number

Relevant Technica	Search Examiner	
(i) UK CI (Edition	L) C3M (MXC); C3V (VEM)	
		A J RUDGE
(ii) Int CI (Edition	5 A63B; C08L	
Databases (see ov	ver)	Date of Search
(i) UK Patent Offic	e	0.6 TANTIATIV 3003
(ii) ONLINE D	ATABASES: WPI, CA SEARCH	26 JANUARY 1993
(ii) ONLINE D	ATABASES: WPI, CA SEARCH	

ALL Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	
х	GB 2247682 A (SPALDING & EVENFLO) - eg page 7 lines 2 -30 and page 12 lines 13-14	All
***************************************	ms - doc99\fil000814	

SF2(p)

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Category	Identity of document and relevant passages	Relevant to claim(s
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Categories of documents

- X: Document indicating lack of novelty or of inventive step.
- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.
- A: Document indicating technological background and/or state of the art.
- P: Document published on or after the declared priority date but before the filing date of the present application.
- E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- &: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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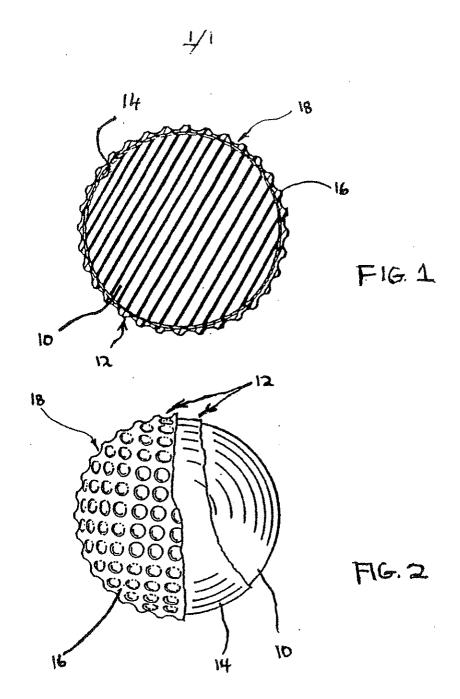
(54) Improved multi-layer golf ball

(57) An improved multi-layer golf ball comprises a core, an inner cover layer and an outer cover layer. The inner cover layer is comprised of a high acid ionomer or ionomer blend which may or may not include a filler such as zinc-stearate. The outer cover layer is comprised of a soft, very low modulus ionomer or ionomer blend, or a non-ionomeric thermoplastic elastomer such as polyurethane, polyester or polyesteramide. The resulting multi-layered golf ball of the present invention provides for enhanced distance without sacrificing playability or durability when compared to known multi-layer golf balls.

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This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.





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IMPROVED HULTI-LAYER GOLF BALL

The present invention relates to golf balls and, more particularly, to improved golf balls comprising multi-layer covers which have a hard inner layer and a relatively soft outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties while at the same time offering the "feel" and spin characteristics associated with soft balata and balata-like covers of the prior art.

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Horeover, the soft balata covers produce a soft "feel" to the low handicap player. Such

playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, trans-polybutadiene and transpolyisoprene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Hemours & Company under the trademark "Surlyne" and more recently, by the Exxon Corporation (see U. S. Patent No. 4,911,451) under the trademarks "Escore" and the trade name "Iotek", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Hetal ions, such as sodium or zinc, are used to neutralize

some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties; i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, while there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of athylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc., a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel", etc.) characteristics previously associated

with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced by the present inventor and others to address these needs. The different types of materials utilized to formulate the cores, covers, etc. of these balls dramatically alters the balls' overall characteristics. In addition, multi-layered covers containing one or more ionomer resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired.

This was addressed by Spalding & Evenflo Companies, Inc.

in U. S. Patent No.

4,431,193 where a multi-layered golf ball is disclosed. In the '193 patent, a multi-layer golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyne (now designated Surlyne 8940). Type 1605 Surlyne (Surlyne 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyne (now designated Surlyne 9020) is molded over the inner cover layer. Type 1855

Surlyn® (Surlyn® 9020) is a zino ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '191 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution The increase in the coefficient of restitution of the core. provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball. Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other known multilayered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls. These undesirable properties make the ball produced in accordance with the '193. patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness

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and durability. As such, the playability characteristics (i.e., "feel", "click", "spin", stc.) are not diminished.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

The present invention is directed to improved multi-layer golf ball cover compositions and the resulting multi-layer golf balls produced using the improved compositions. The novel multi-layer golf ball covers of the present invention include a first or inner layer or ply of a high acid (greater than 16 weight percent acid) ionomer or ionomer blend and second or outer layer or ply comprised of a comparatively softer, low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic elastomer such as polyurethane, a polyester alastomer such as Hytrel® polyester elastomer of E.I. DuPont de Hemours & Company, or a polyesteramide such as the Elf Atochem S.A. Pebax® polyesteramide. Preferably, the outer cover layer includes a blend of hard and soft low acid (i.e. 16 weight percent acid or less) ionomers.

It has been found that the recently developed high acid ionomer based inner layer, provides for a substantial increase in resilience (i.e., enhanced distance) over known multi-layer covered balls. The softer outer layer provides for desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and increases the area of contact between the club face and the cover,

thereby imparting more spin on the ball. As a result, the soft cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability. Consequently, the overall combination of the inner and outer cover layers results in a golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

The combination of a high acid ionomer or ionomer blend inner cover layer with a soft, relatively low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic elastomer outer cover layer provides for excellent overall coefficient of restitution (i.e., excellent resilience) because of the improved resiliency produced by the inner cover layer. While some improvement in resiliency is also produced by the outer cover layer, the outer cover layer generally provides for a more desirable feel and high spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

balls is a function of the composition of the molded core and of the cover. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the slastomeric windings. Although both the core and the cover contribute to the coefficient of restitution, the present invention is directed to the enhanced coefficient of restitution (and thus travel distance) which is affected by the cover composition.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States

Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Patent No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples.

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer

cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances, improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

These and other objects and features of the invention will be apparent from the following detailed description and the accompanying drawings which are by way of example.

FIG. 1 is a cross-sectional view of a golf ball embodying the invention illustrating a core 10 and a cover 12 consisting of an inner layer 14 and an outer layer 16 having dimples 18; and

FIG. 2 is a diametrical cross-sectional view of a golf ball of the invention having a core 10 and a cover 12 made of an inner layer 14 and an outer layer 16 having dimples18.

The present invention relates to improved multi-layer golf balls, particularly a golf ball comprising a multi-layered cover 12 over a solid core 10, and method for making same.

The multi-layered cover 12 comprises two layers: a first or inner layer or ply 14 and a second or outer layer or ply 16. The inner layer 14 is comprised of a high acid (i.e. greater than 16 weight percent acid) ionomer resin or high acid ionomer blend. Preferably, the inner layer is comprised of a blend of two or more high acid (i.e. at least 16 weight percent acid) ionomer resin neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the

metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

The inner layer compositions include the high acid ionomers such as those recently developed by E. I. DuPont de Nemours & Company under the trademark "Surlyne" and by Exxon Corporation under the trademark "Escore" or tradename "Totak", or blends thereof. Examples of compositions which may be used as the inner layer herein are set forth in detail in copending U. s. Serial No. 07/776,803 filed October 15, 1991, and Serial No. 07/901,660 filed June 19, 1992, both incorporated herein by Of course, the inner layer high acid ionomer reference. compositions are not limited in any way to those compositions set forth in said copending applications. For example, the high acid ionomer resins recently developed by Spalding & Evenflo Companies. Inc., the assignee of the present invention, and disclosed in U.S. Serial Ho. 07/901,680, filed June 19, 1992, incorporated herein by reference, may also be utilized to produce the inner layer of the multi-layer cover used in the present invention.

The high acid ionomers which may be suitable for use in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resine are copolymers of ethylene and either acrylic or

methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10-75%, preferably 30-70%) by the metal ions. Each of the high acid ionomer resins which may be included in the inner layer cover compositions of the invention contains greater than about 16% by weight of a carboxylic acid, preferably from about 17% to about 25% by weight of a carboxylic acid, more preferably from about 18.5% to about 21.5% by weight of a carboxylic acid, more preferably from about 18.5% to about 21.5% by weight of a carboxylic acid.

Although the inner layer cover composition preferably includes a high acid ionomeric resin and the scope of the patent embraces all known high acid ionomeric resins falling within the parameters set forth above, only a relatively limited number of these high acid ionomeric resins have recently become commercially available.

The high acid ionomeric resins available from Exxon under the designation "Escore" and or "Iotek", are somewhat similar to the high acid ionomeric resins available under the "Surlyne" trademark. However, since the Escore/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the "Surlyne" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

Examples of the high acid methacrylic acid based ionomers found suitable for use in accordance with this invention include

Surlyn® AD-8422 (sodium cation), Surlyn® 8162 (zinc cation), Surlyn® SEP-503-1 (zinc cation), and Surlyn® SEP-503-2 (magnesium cation). According to DuPont, all of these ionomers contain from about 18.5 to about 21.5% by weight methacrylic acid.

Hore particularly, Surlyn® AD-8422 is currently commercially available from DuPont in a number of different grades (i.e., AD-8422-2, AD-8422-3, AD-8422-5, etc.) based upon differences in melt index. According to DuPont, Surlyn® AD-8422 offers the following general properties when compared to Surlyn®8920, the stiffest, hardest of all on the low acid grades (referred to as "hard" ionomers in U.S. Patent No. 4,884,814):

	TOH YCID	HIGH ACLD			
(15 wt\ Acid}	(>20	wtl Acid)		
	SURLYN•	SURLYNO	SURLYNO		
	8920	8422-2	8422-3		
10HOHER					
Cation	Na	Na	Na		
Melt Index	1.2	2.8	1.0		
sodium, Wtł	2.3	1.9	2.4		
Base Resin MI	60	60	60		
HP ¹ , °C	88	86	8.5		
FP ¹ , *C	47	48.5	45		
COMPRESSION MO	rdi Mg³				
Tensile Break,					
psi	4350	4190	5330		
Yleld, psi	2880	3670	3590		
Elongation, & Flex Hod,	315	263	289		
K psi	53.2	76.4	88.3		

_ 1	12	

Shore D			
hardness	66	67	68

DSC second heat, 10°C/min heating rate.
Samples compression molded at 150°C annealed 24 hours at 60°C. 8422-2, -3 were homogenized at 190°C before molding.

In comparing Surlyn® 8920 to Surlyn® 8422-2 and Surlyn® 8422-3, it is noted that the high acid Surlyn® 8422-2 and 8422-3 ionomers have a higher tensile yield, lower elongation, slightly higher Shore D hardness and much higher flexural modulus. Surlyn® 8920 contains 15 weight percent methacrylic acid and is 59% neutralized with sodium.

In addition, Surlyn® SEP-503-1 (zinc cation) and Surlyn® SEP-503-2 (magnesium cation) are high acid zinc and magnesium versions of the Surlyn® AD 8422 high acid ionomers. When compared to the Surlyn® AD 8422 high acid ionomers, the Surlyn® SEP-503-1 and SEP-503-2 ionomers can be defined as follows:

Surlyn® Ionomer	Ion	Melt Index	Neutralization 1
AD 8422-3	Na	1.0	45
SEP 503-1	Zn	0.8	38
SEP 503-2	Mg	1.8	43

Furthermore, Surlyn® 8162 is a zinc cation ionomer resin containing approximately 20% by weight (i.e. 18.5-21.5% weight) methacrylic acid copolymer that has been 30-70% neutralized. Surlyn® 8162 is currently commercially available from DuPont.

Examples of the high acid acrylic acid based ionomers suitable for use in the present invention also include the Escor® or lotek high acid ethylene acrylic acid ionomers produced by

Exxon. In this regard, Escor® or lotek 959 is a sodium ion neutralized ethylena-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, loteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 10 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

BUCHESIA	ESCOR* (101EK) 959	ESCORP (HOTEK) 960
Heit Index, g/10 min	2.0	1.8
Estion	# odfum	linc
Kelting Point, "F	172	174
Vicat Softening Point, *f	130	131
Tensite B Break, pai	4800	3500
Elongation & Break, X	325	430
Barchess, Shore D	åå	57
Plexurat Modulus, psi	66,000	27,000

Furthermore, as a result of the development by the inventor of a number of new high acid ionomers neutralized to various extents by several different types of metal cations, such as by manganese, lithium, potassium, calcium and nickel cations, several new high acid ionomers and/or high acid ionomer blends besides sodium, zinc and magnesium high acid ionomers or ionomer blends are now available for golf ball cover production. It has been found that these new cation neutralized high acid ionomer blends produce inner cover layer compositions exhibiting enhanced hardness and resilience due to synergies which occur during

processing. Consequently, the metal cation neutralized high acid ionomer resins recently produced can be blended to produce substantially harder inner cover layers for multi-layered golf balls having higher C.O.R.'s than those produced by the low acid ionomer inner cover compositions presently commercially available.

More particularly, several new metal cation neutralized high acid ionomer resins have been produced by the inventor by neutralizing, to various extents, high acid copolymers of an alphalolefin and an alpha, beta-unsaturated carboxylic acid with a wide variety of different metal cation salts. This discovery is the subject matter of U.S. Application Serial No. 901,680, incorporated herein by reference. It has been found that numerous new metal cation neutralized high acid ionomer resins can be obtained by reacting a high acid copolymer (i.e. a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid), with a metal cation salt capable of ionizing or neutralizing the copolymer to the extent desired (i.e. from about 10% to 90%).

The base copolymer is made up of greater than 16t by weight of an alpha, beta-unsaturated carboxylic acid and an alphaolefin. Optionally, a softening comonomer can be included in the
copolymer. Generally, the alpha-olefin has from 2 to 10 carbon
atoms and is preferably ethylene, and the unsaturated carboxylic
acid is a carboxylic acid having from about 3 to 8 carbons.
Examples of such acids include acrylic acid, methacrylic acid,

ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred.

The softening comonomer that can be optionally included in the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high acid ionomers included in the present invention include, but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/malaic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an athylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 30 to about 83% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

Along these lines, examples of the preferred high acid base copolymers which fulfill the criteria set forth above, are a series of ethylene-acrylic copolymers which are commercially available from The Dow Chemical Company, Midland, Michigan, under the "Primacor" designation. These high acid base copolymers exhibit the typical properties set forth below in Table 1.

TABLE 1
Typical Properties of Primacor
Ethylene-Acrylic Acid Copolymers

CEADE .	PEACENT ACID	DEHEETY, gicc	MELT INOCK, g/lowin	TENSILE YD. ST (p=1)	FLEXURAL MODULUS (ps1)	(,c) soli .bi Alcyi	SHORE D
ASTM		0-792	D-1238	8-638	0-790	0-1525	D-2240
5980	20.0	0.958	300.0	•	4800	43	50
5990 5990	20.0 20.0	0.955 0.955	1300.0 1300.0	659 650	3500 5600	40	42 62
5981 5981	20.0	0.960 0.960	300.0 300.0	900 900	3200 3200	46 45	48 48
- 5983	20.0	0.956	500.0	850	3100	44	45
5991	20.0	0.953	2600.0	635	2600	38	40

"The Held Index values are obtained according to ASTM 0-1238, at 190°C.

Due to the high molecular weight of the Primacor 5981 grade of the ethylene-acrylic acid copolymer, this copolymer is the more preferred grade utilized in the invention.

The metal cation salts utilized in the invention are those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide

salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The new metal cation neutralized high acid ionomer resins are produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200° F to about 500° F, preferably from about 250° F to about 350° F under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in

the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

As indicated below in Table 2 and more specifically in Example 1 in U.S. Application Serial No. 901,680, a number of new types of metal cation neutralized high acid ionomers can be obtained from the above indicated process. These include new high acid ionomer resins neutralized to various extents with manganese, lithium, potassium, calcium and nickel cations. In addition, when a high acid ethylene/acrylic acid copolymer is utilized as the base copolymer component of the invention and this component is subsequently neutralized to various extents with the metal cation salts producing acrylic acid based high acid ionomer resins neutralized with cations such as sodium, potassium, lithium, zinc, magnesium, manganese, calcium and nickel, several new cation neutralized acrylic acid based high acid ionomer resins are produced.

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TABLE 2

formulation Ho.	UL-X Cation Sait	We-X Revised lies for	Hell Index	C.O.R.	Shore D Reidness
(KROR)	6.98	67.\$	0,9	.804	71
2(NaOH)	3.66	\$4.0	2.4	.808	73
31HaOH)	3.84	35.9	12.2	.612	69
'4(R6GR)	19.5	27.0	17.5	.812	(brittle)
S(HrAc)	19.6	71.7	7.5	.809	73
6(KrAc)	23.1	88.3	3.5	.814	n
7(HALE)	15.3	53.0	7.5	.810	72
B(HnAc)	26.5	106	0.7	.813	(brittle)
P(LEGH)	4.54	71.3	0.6	.810	74
_ (Hal 3) 01	3.38	52.5	4.2	.818	72
11(E 10H)	2.34	35.9	18.6.	.845	72
15(kOH)	5.30	36.0	19.3	Broke	70
13(KOH)	8.26	57.9	7.18	.804	70
14 (KON)	10.7	77.0	4.3	.801	67
15(2ntc)	17.9	71.5	0.2	.808	71
16(2nAc)	13.9	. 53.0	8.9	.797	69
17(2nAc)	9.71	36.1	3.4	. 793	67
18(MgAc)	\$7.4	70.7	8.5	.814	74
19(HgAc)	20.6	87.1	1.5	.815	76
(akgk105	13.8	53.0	4.1	.814	74
21(CaAc)	13.2	69.2	1.1	.813	74
22(CaAc)	7.12	34.9	10.1	.805	70

Controls:

50/50 Blend of Soteks 8000/7030 C.O.R. -. 810/65 Shore D Hardness DuPont High Acid Suriyy 8472 (No.) C.O.R. -. 811/70 Shore D Hardness DuPont High Acid Suriyy 8162 (2n) C.O.R. -. 807/65 Shore D Hardness Exxon High Acid Sotek EX-960 (2n) C.O.R. -. 794/65 Shore D Hardness

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TABLE 2 (continued)

formulation Ho.	Ut-X Cation Salt	Hentlafflution	Helt Index	£.0.2.
23 (HgO)	2.91	53.5	2.5	.513
24 (HgO)	3.85	71.5	. 2.6	.808
2\$ (NgO)	4.76	89.3	1.1	.809
26(MgC)	1.96	35.7	7.5	.815

Control for Formulations 23-26 is \$0/50 lotek 8000/7030, C.O.A. *.814, formulation 26 C.O.A. was normalized to that control accordingly

TABLE 2 (continued)

formulation Ho.	W(-X Cation Salt	Mentrelization	Helt Index	<u>C.O.R.</u>	there p
27(HiAc) .	13.04	61.1	. 0.2	.802	71
SECKEYC)	10.71	48.9	0.8	.799	72
Sa(Riye)	8.26	36.7	1.8	.796	69
3D(NIAc)	5.66	24.4	7.5	.786	64

Control for formulation Box. 27-30 is 50/50 lotek 8000/7030, E.O.R.=.807

When compared to low acid versions of similar cation neutralized ionomer resins, the new metal cation neutralized high acid ionomer resins exhibit enhanced hardness, modulus and resilience characteristics. These are properties that are particularly desirable in a number of thermoplastic fields, including the field of golf ball manufacturing.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the new acrylic acid based high acid ionomers extend the range of hardness beyond that previously obtainable while maintaining the beneficial properties (i.e. durability, click, feel, etc.) of the softer low acid ionomer covered balls, such as balls produced utilizing the

low acid ionomers disclosed in U.S. Patent Nos. 4,884,814 and 4,911,451.

Horeover, as a result of the development of a number of new acrylic acid based high acid ionomer resins nautralized to various extents by several different types of metal cations, such as manganese, lithium, potassium, calcium and nickel cations, several new ionomers or ionomer blends are now available for production of an inner cover layer of a multi-layered golf ball. By using these high acid ionomer resins, harder, stiffer inner cover layers having higher C.O.R.'s, and thus longer distance, can be obtained.

More preferably, it has been found that when two or more of the above-indicated high acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further than previously known multi-layered golf balls produced with low acid ionomer resin covers due to the balls' enhanced coefficient of restitution values.

For example, the multi-layer golf ball taught in 4,650,193 does not incorporate a high acid ionomeric resin in the inner cover layer. As will be set forth below in the Examples, the coefficient of restitution of the golf ball having an inner layer taught by the '193 patent (i.e., inner layer composition "p" in the Examples) is substantially lower than the coefficient of restitution of the remaining compositions. In addition, the multi-

layered ball disclosed in the '193 patent suffers substantially in durability in comparison with the present invention.

With respect to the outer layer 16 of the multi-layered cover of the present invention, the outer cover layer is comparatively softer than the high acid ionomer based inner layer. The softness provides for the feel and playability characteristics typically associated with balata or balata-blend balls. The outer layer or ply is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,000 psi) and low acid (less than 16 weight ionomer, ionomer blend or a non-ionomeric percent acid) thermoplastic elastomer such as, but not limited to, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, or a polyester amide such as that marketed by Elf Atochem S.A. under the trademark Pebax*. The outer layer is fairly thin (i.e. from about 0.010 to about 0.050 in thickness, more desirably 0.03 inches in thickness for a 1.680 inch but thick enough to achieve desired playability ball). characteristics while minimizing expense.

Preferably, the outer layer includes a blend of hard and soft (low acid) ionomer resins such as those described in U. S. Patent Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Specifically, a desirable material for use in molding the outer layer comprises a blend of a high modulus (hard) ionomer with a low modulus (soft) ionomer to form a base ionomer mixture. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance with ASTM

method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTH method D-2240.

A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15-75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation "lotek" are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the "lotek" ionomeric resins are sodium or sinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some distinct differences in

properties exist. As more specifically indicated in the data set forth below, the hard "lotek" resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the outer layer blends for use in the present invention. In addition, various blends of "lotek" and Surlyn* hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the outer cover blends include the hard sodium ionic copolymer sold under the trademark Surlyn®8940 and the hard zinc ionic copolymer sold under the trademark Surlyn®8940. Surlyn®8940 is a copolymer of athylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. This resin has an average melt flow index of about 2.8. Surlyn®9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn®9910 is about 0.7. The typical properties of Surlyn®9910 and 8940 are set forth below in Table 3:

-27-

TABLE 3

Typical Properties of Commercially Available Hard

Surlyn® Resins Suitable for Use in the Outer Layer Blends of

	the Present Invention						
	ASTH P	8950	22.10	8920	5575	2279	2729
Cation Type	•	\$ odium	2 fnc	todius	Sodius	2 fnc	Zinc
Helt flow Index, grs/10 mln.	D · 1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, 9/cm ²	D-792	0.95	0.67	0.95	0.94	0.95	0.95
Rardness, Shore D	p-3240	66	64	66	60	62	43
Tensile Strength, (kpsi), KPa	D-638	(1.8) 35.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(1.1) 28.0
Elongation, E	D-638	470	290	350	450	460	460
Figurat Modulus, (hpsi) MPa	p-790 ,	(31) 350	(48) 330	(55) 380	550 (35)	(28) 190	\$10 {36}
Bensile import (23°C) El/m, (it. lbs./in')	0-16228	1070 (485)	1020 (485)	845 (410)	1160 (530)	760 (360)	1240 (590)
Vicat Temperature, "C	D-1585	43	62	56	73	61	73

Examples of the more pertinent acrylic acid based hard ionomer resin suitable for use in the present outer cover composition sold under the "Iotek" tradename by the Exxon Corporation include Iotek 4000, Iotek 4010, Iotek 8000, Iotek 8020 and Iotek 8030. The typical properties of these and other Iotek hard ionomers suited for use in formulating the outer layer cover composition are set forth below in Table 4:

-28-

TABLE 4

Typical Properties of Totek Ionomers

Recin	AS	H						
Properties	Hs	thed	Moite	4000	6010	8000	8020	8010
Cation type				1 Inc	tina	rodius	sodium	sodius
Helt Index	٥-	1238	g/10 min.	2.5	1.5	8.4	1.6	2.8
Density	9-	1505	kg/m³	963	963	954	960	960
Helting Point	D-	3417	*c	90	90	90	87.5	87.5
Crystallization	Point b-	34 17	' C	65	64	56	53	55
Vicat Softening	Point D-	1525	' C	62	63	61	64	67
A Weight Acrylic	Acid			14		11		
X of Acid Groups cation neutralize	ed.			30		40		
Plaque Properties (3 mm thick, compression motific	-	in thod	Unite	6000	4019	<u>8000</u>	6020	8030
Tenzite at break	9-6	38	нра	24	26	36	31.5	28
Tield point	D-6	38	HPe .	none	none	21	21	23
Elangetian et bro	ak D-6	38	x	395	420	350	410	395
1% Secant modulus	b-6	38	KPa	160	160	300	350	390
Shore Herdness 9	5-5	240	••	55	55	61	58	59
Film Properties (50 micron (lim) Blow-up (stio)	.2:1			4000	<u>4010</u>	8000	8020	8030
Ienzile at Breek	ND D-8	LA?	HPa.	41	39			
	10 9-8		MP a	37	38	42 38	52 38	47.4 40.5
Yield point	5-0 OH 5-0 OH		MPs MPs	15 14	17 15	87 15	51 53	21.6 20.7
Elangation at Bro	ak							
	10 D-6		Ä	310	270	260	295	305
	10 0-8	10 K	ı	360	340	085	340	345
1X Secant modulus			HPs.	210	215	390	380	OBE
	10 D-8	182	HPs	200	552	340	350	345
Dark Drop Impact	D-1	709	g/steron	12.4	12.5	20.3		

	•				
Scala Preservita	At th Kelhod	Vnita	7019	<u>76</u> 29	2010
Ceston type			a inc	zino	zinc
Hell Irdex	D-1234	g/10 mln.	9.6	1.5	2.5
Density	9 - 1503	kg/m²	949	960	866
Helting Point	p-3417	٠,٤	90	90	95
Erystattisation Faint	p-3617	*c		~~	
Vical Softening Point	p · 1525	٠٤	60	43	42.5
meight Acrylle Acid	í		•-		• •
I of Acid Groups Callon Revitabled				••	
Plaque Plagestiff (I ma thick, corpression molded)	<u>Rethod</u> Yf in	Ynlia Ynlia	7919	<u> 1020</u>	7939
lensite at break	816-0	MPa	38	ys	30
Held Folns	8£à-6∵,÷≒	HP a	non4	none	PORIE
Elongation at break	0-618	x	300	620	395
\$2 Secant produkus	863·G	biP a	••		••
Shore Hardness D	0-5340	••	57	55	35

Comparatively, soft ionomers are used in formulating the hard/soft blends of the outer cover composition. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an elefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the scrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on

the Shore D scale and a flexural modulus from about 1,000 to about 10,000, as measured in accordance with ASTH method D-790.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation "Iotek 7520" (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the outer cover. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects) as well as significant cost savings versus the outer layer of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials costs and improved yields.

While the exact chemical composition of the resins to be sold by Exxon under the designation lotek 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

-31-TABLE 5

Physical Properties of Totak 7520

Property	ASTM Method	Units	Typical Value
Helt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m³	0.962
Cation			zinc
Helting Point	D-3417	*C	66
Crystallization Point	D-3417	•c	49
Vicat Softening Point	D-1525	° C	42

Plaque Properties 12 mm thick Compression Holded Plaques)

Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	Hone
Elongation at Break	D-638	ŧ	760
1% Secant Hodulus	D-638	MPa	2 2
Shore D Hardness	D-2240	•	32
Flexural Hodulus	D-790	MPa	26
Zwick Rebond	ISO 4862	. *	52
De Hattia Flex Resistance	D-430	Cycles	>5000

In addition, test data collected by the inventor indicates that lotek 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTH D-2240), melt flow indexes of 3±0.5 g/10 min (at 190°C. per ASTH D-1288), and a flexural modulus of about 2500-3500 psi (per ASTH D-790). Furthermore, testing by an independent

testing laboratory by pyrolysis mass spectrometry indicates that Iotek 7520 resins are generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, the inventor has found that a newly developed grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation lotek 7510, is also effective, when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, lotek 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the lotek 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn 8625 and the Surlyn 8629 combinations disclosed in U.S. Patent No. 4,884,814).

In addition, Totek 7510, when compared to Totek 7520, produces slightly higher C.O.R. valves at equal softness/hardness due to the Totek 7510's higher hardness and neutralization. Similarly, Totek 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than Totek 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, Totak 7510 is of similar chemical composition as Totak 7520 (i.e. a zinc salt of a terpologmer of athylene, acrylic acid, and methyl acrylate) but is more highly

neutralized. Based upon FTIR analysis, Iotek 7520 is estimated to be about 30-40 wt.-% neutralized and Iotek 7510 is estimated to be about 40-60 wt.-% neutralized. The typical properties of Iotek 7510 in comparison of those of Iotek 7520 are set forth below:

Physical Properties of Intel 7510 In Comparison to lotek 7520

	<u>10TEK 7520</u>	<u>10TEK 7510</u>
HI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Helting Point, °F	151	149
Vicat Softening Point, °F	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

Specific formulations which may be used in the cover composition are included in the examples set forth in U. S. Patent No. 5,120,791 and 4,884,814. The present invention is in no way limited to those examples.

Horeover, in alternative embodiments, the outer cover layer formulation may also comprise a soft, low modulus non-ionomeric thermoplastic elastomer including a polyester polyurethane such as B.F.Goodrich Company's Estane® polyester polyurethane X-4517. According to B.F.Goodrich, Estane® X-4517 has the following properties:

Properties of Estane® X-4517

•	
Tensile	1430
100%	815
2001	1024
300%	1193
Elongation	641
Youngs Modulus	1826
Hardness A/D	88/39
Dayshore Rebound	59
Solubility in Water	Insoluble
Helt processing temperature	>350°F (>177°C)
Specific Gravity (H,O=1)	1.1-1.3

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced travel distance characteristic produced by the high acid ionomer resin composition.

These include, but are not limited to thermoplastic polyurethanes such as: Texin thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane thermoplastic polyurethanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Patents 4,986,545; 5,098,105 and 5,187,013; and, Hytrel polyester elastomers from DuPont and pebax polyesteramides from Elf Atochem 5.A.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core). A comparatively softer outer layer is molded over the inner layer.

The conventional solid cors is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid corss are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an a, \(\theta\), ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty

acids such as stearic acid. Free radical initiators such as peroxides are admixed with the core composition so that on the application of heat and pressure, a complex curing cross-linking reaction takes place.

The inner cover layer which is molded over the core is about 0.100 inches to about 0.010 inches in thickness, preferably about 0.0375 inches thick. The outer cover layer is about 0.010 inches to about 0.050 inches in thickness, preferably 0.0300 inches thick. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or more, the minimum diameter permitted by the rules of the United States Golf Association and weighing about 1.620 ounces.

Additional materials may be added to the cover compositions (both inner and outer cover layer) of the present invention including dyes (for example, Ultramarine Blue sold by Whitaker, Clark and Daniels of South Plainsfield, N.J.) (see U.S. Patent No. 4,679,795); pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; and UV absorbers; antioxidants; antistatic agents; and stabilizers. Further, the cover compositions of the present invention may also contain softening agents, such as plasticizers, processing aids, etc. and reinforcing material such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers are not impaired.

The various cover composition layers of the present invention may be produced according to conventional melt blending

procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the high acid ionomer resin compositions used to produce the inner cover layer.

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

In compression molding, the inner cover composition is formed via injection at about 380°F to about 450°F into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 300°F for about 2 to 10 minutes, followed by cooling at 50° to 70°F for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50°F to about 100°F. Subsequently, the outer cover layer is molded about the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Patent No. 4,911,451.

The resulting golf ball produced from the high acid ionomer resin inner layer and the relatively softer, low flexural modulus outer layer provide for an improved multi-layer golf ball which provides for desirable coefficient of restitution and durability properties while at the same time offering the feel and spin characteristics associated with soft balata and balata-like covers of the prior art.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

Examples

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc discrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about .800. A representative formulation of the molded cores is set forth below:

HATERIAL	WEIGHT
BR-122G (high cis-polybutadiene)	70.70
Taktene 220 (high cis-polybutediene)	29.30
React Rite 2DA (sinc discrylate)	31.14
Zinc Oxide	6.23
ling Stearate	20, 15
(imestons	17.58
Ground Flash	20,15

-40-

120-40 Hesh)

Rius Kasterbatch

.012

Luperco 231XL or Trigonox 29/40

.89

Popl 94

.50

"Blue Masterbatch consists of unknown compositions used only for internal identification purposes and has no eilect on physical properties.

inner cover compositions designated herein as compositions A-E utilized to formulate the intermediate balls are The resulting molded intermediate set forth in Table 7 below. balls were tested to determine the individual compression (Richle), C.O.R., Shore C hardness, spin rate and cut resistance properties. These results are also set forth in Table 7 below.

The data of these examples are the average of twelve intermediate balls produced for each example. The properties were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air canon at a velocity of 125 feet per second against a steel plate positioned 12 feet from the muzzle of the canon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give a coefficient of restitution.

Shore hardness was measured in accordance with ASTM test 2240.

Cut resistance was measured in accordance with the following procedure: A golf ball is fired at 135 feet per second against the leading edge of a pitching wedge wherein the leading edge radius is 1/32 inch, the loft angle is 51 degrees, the sole radius is 2.5 inches and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 to 5. The number 1 represents a cut that extends completely through the cover to the A 2 represents a cut that does not extend completely through the cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins, with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn 1605) used in U.S. Patent No. 4,431,193. Composition B provides a hard, low acid ionomeric resin.

The purpose behind producing and testing the balls of Table IV was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.

Table 7
Holded Intermediate Golf Balls

Ingredients of Inner Cover Compositions	ı A	В	£	Ω	£
lotek 959	50	´ 50			-
lotek 960	50	50	***		
2inc Stearate		50	 ,		
Surlyn 8162			75		
Surlyn 8422			25		
Surlyn 1605	~~		-	100	

	-	-42-			
Totek 7030	mir des				50
lotek 8000			~-		50
Properties of Holded Intermediate Balls					
Compression	58	58	60	63	62
C.O.R.	.811	.810	.807	.793	.801
Shore C Hardness	98	9.8	97	96	96
Spin Rate (R.P.H.)	7,367	6,250	7,903	8,337	7,956
Cut Resistance	4-5	4-5	4-5	4-5	4-5

As shown in Table 7 above, the high acid ionomer resin inner cover layer (molded intermediate balls A-C) have lower spin rates and exhibit substantially higher resiliency characteristics than the low acid ionomer resin based inner cover layers of balls D and E.

Hulti-layer balls in accordance with the present invention were then prepared. Specifically, the inner cover compositions used to produce intermediate golf balls from Table 7 were molded over the solid cores to a thickness of about 0.0375 inches, thus forming the inner layer. The diameter of the solid core with the inner layer measured about 1.620 inches. Alternatively, the intermediate golf balls of Table 7 were ground down using a centerless grinding machine to a size of 1.620 inches in diameter to produce an inner cover layer of 0.0375 inches.

The size of 1.620 inches was determined after attempting to mold the outer cover layer to various sizes (1.600", 1.610", 1.620", 1.630" and 1.640") of intermediate (core plus inner layer) balls. It was determined that 1.620" was about the largest "intermediate" ball (i.e., core plus inner layer) which could be easily molded over with the soft outer layer materials of choice.

The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials. However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

with the above in mind, an outer cover layer composition was blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Patent No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth as follows:

Outer Cover Layer Composition TE-90

Iotek	8000	22.7	weight	*
Iotek		22.7	weight	ŧ
Iotak		45.0	weight	*
White		9.6	weight	à

White MB consists of about 23.77 weight percent TiO;; 0.22 weight percent Uvitex OB, 0.03 weight percent Santonox R, 0.05 weight percent Ultramarine blue and 75.85 weight percent lotek 7030.

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A-D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D

(the intermediate ball representative of the '193 patent). The outer layer TE-90 was molded to a thickness of approximately 0.030 inches to produce a golf ball of approximately 1.680 inches in diameter. The resulting balls (a dozen balls for each example) were tested and the various properties thereof are set forth in Table 8 as follows:

Table 8
Finished Balls

ingredients:	_1_		1	_5_	_3_
inner Cover Coopasition	A		c	b	D
Outer Cover Composition	TE-90	1E-90	16-90	\$E-90	Sur 1 yrre 9020
Properties of Moided Finished Sails:					
Compression	63	63	69	70	61
E.O.8.	.784	.778	.780	.770	.757
Shore C Hardness	85	88	88	88	89
Spin (R.P.X.)	8,825	8,854	8,814	8,990	8,846
Eut Resistance	3-4	3-4	3-4	3-4	1-2

As it will be noted in finished balls 1-4, by creating a multi-layer cover utilizing the high acid ionomer resins in the inner cover layer and the hard/soft low acid ionomer resin in the outer cover layer, higher compression and increased spin rates are noted over the single layer covers of Table 7. In addition, both the C.O.R. and the Shore C hardness are reduced over the respective single layer covers of Table IV. This was once again particularly true with respect to the multi-layered balls containing the high

acid ionomer resin in the inner layer (i.e. finished balls 1-5). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased. As note above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the present invention.

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1-3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B.F.Goodrich Estane® X-4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn®9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table VI below:

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Table 9
Finish Balls

Ingredientes	_6_	
Irner Cover Layer Composition	A	0
Outer Cover Layer Composition	Estanes 4517	Surlyne 9020
Properties of Moided Finished Bails:		·
Coopression	67	61
C.O.R.	.774	.757
Shore C Hardmans	74	89
Spin (R.P.M.)	10,061	8,846
Cut Resistance	3-4	1-2

The ball comprising inner layer formulation D and Surlyne 9020 identifies the ball in the Nesbitt 4,431,193 patent. As is noted, the example provides for relatively high softness and spin rate though it suffers from poor cut resistance and low C.O.R. This ball is unacceptable by today's standards.

As for the Estane® X-4517 polyester polyurethans, a significant increase in spin rate over the TE-90 cover is noted along with an increased compression. However, the C.O.R. and Shore C values are reduced, while the cut resistance remains the same. Furthermore, both the Estane® X-4517 polyester polyurathane and the Surlyn® 9020 were relatively difficult to mold in such thin sections.

The invention has been described with reference to the preferred embodiment. Modifications and alterations will occur to others upon reading and understanding the proceeding

detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

The qualifications "about" and "substantially" include the precise values, and precise values include values about or substantially the same as the precise values.

The present disclosure includes the foregoing description, and the appended claims, drawings, and abstract.

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CLAIMS

1. A golf ball comprising:

a core;

an inner cover layer molded on said core, the inner cover layer comprising a high acid ionomer including at least 16% by weight of an alpha, beta-unsaturated carboxylic acid; and

an outer cover layer molded on said inner cover layer, said outer cover layer comprising a relatively soft polymeric material selected from the group consisting of low flexural modulus ionomer rasins and non-ionomeric thermoplastic elastomers.

- 2. A golf ball according to claim 1 wherein the inner cover layer comprises a high acid ionomer resin comprising a copolymer of about 17% to about 25% by weight of an alpha, beta-unsaturated carboxylic acid.
- 3. A golf ball according to claim 1 wherein the inner cover layer comprises a high acid innomer resin comprising a copolymer of about 18.5% to about 21.5% by weight of an alpha, beta-unsaturated carboxylic acid.
- 4. A golf ball according to claim 1, wherein the inner cover layer has a thickness of about 0.100 to about 0.010 inches and the outer cover layer has a thickness of about 0.010 to about

0.05 inches, the golf ball having an overall diameter of 1.680 inches or more.

- 5. A golf ball according to claim 1 wherein the inner cover layer has a thickness of about 0.300 inches and the outer cover layer has a thickness of about 0.375 inches, the golf ball having an overall diameter of 1.680 inches or more.
- 6. A golf ball according to claim 1 wherein the outer layer comprises a low flexural modulus ionomer resin which includes a blend of a hard high modulus ionomer with a soft low modulus ionomer, the high modulus ionomer being a sodium, zinc, magnesium or lithium salt of a copolymer having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms, the low modulus ionomer being a sodium or zinc salt of a terpolymer of an olefin having 2 to 8 carbon atoms, acrylic acid and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms.
- 7. A golf ball according to claim 6 wherein the outer layer composition includes 90 to 10 percent by weight of the hard high modulus ionomer resin and about 10 to 90 percent by weight of the soft low modulus ionomer resin.
- 8. A golf ball according to claim 6 wherein the outer layer composition includes 75 to 25 percent by weight of the hard

high modulus ionomer resin and about 25 to 75 percent by weight of the soft low modulus ionomer resin.

- 9. A golf ball according to claim 1 wherein the non-ionomeric thermoplastic elastomer is a polyester polyurethane.
- 10. A golf ball according to claim 1 wherein the non-ionomeric thermoplastic elastomer is a polyester elastomer.
- 11. A golf ball according to claim 1 wherein the non-ionomeric thermoplastic elastomer is a polyester amide.
 - 12. A multi-layer golf ball comprising: a spherical cora;

an inner cover layer molded over said spherical core, said inner cover layer comprising an ionomeric resin including at least 16% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi;

an outer cover layer molded over said spherical intermediate ball to form a multi-layer golf ball, the outer layer comprising a blend of i) a sodium or zinc salt of a copolymer having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms, and ii) a sodium or zinc salt of a terpolymer of an olefin having 2 to 8 carbon atoms, acrylic acid and an unsaturated monomer of the

acrylate ester class having from 1 to 21 carbon atoms, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi.

13. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer molded over said spherical core to form a spherical intermediate ball, said inner cover layer comprising an ionomeric resin including about 17% to about 25% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi;

an outer cover layer molded over said spherical intermediate ball to form a multi-layer golf ball, the outer layer comprising a non-ionomeric thermoplastic selected from the group consisting of polyester elastomer, polyester polyurethane and polyester amide, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi.

- an inner cover layer and an outer cover layer, wherein the inner cover layer is comprised of a high acid ionomer or ionomer blend which may or may not include a filler (e.g. zinc-stearate), and the outer cover layer is comprised of a soft, very low modulus ionomer or ionomer blend, or a non-ionomeric thermoplastic elastomer (e.g. polyurethane, polyester, or polyesteramide.
- 15. A golf ball according to claim 1, substantially as hereinbefore described.
- 16. A golf ball according to claim 12, substantially as hereinbefore described.
- 17. A golf ball according to claim 13, substantially as hereinbefore described.
- 18. A golf ball according to claim 14, substantially as hereinbefore described.
- 19. A golf ball, substantially as hereinbefore described with reference to and as shown in the accompanying drawings.



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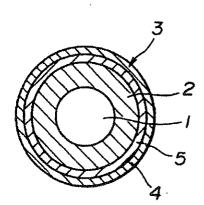
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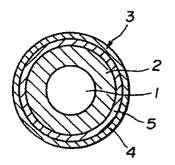
(54) Wound golf ball

(57) In a wound golf ball comprising a liquid center (1), thread rubber (2), and a cover (3), the cover has a multilayer structure including an outer layer (4) and an inner layer (5) having a higher hardness than the outer layer. The outer layer (4) is 0.4 - 3.0 mm thick. The ball affords improved spin and flying distance and is fully FIG.1



1/1

FIG.1



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2291811

Wound Golf Ball

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This invention relates to a thread wound golf ball which is durable while affording a satisfactory flying distance and controllability.

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Prior art thread wound golf balls with a solid center have two types of covers, that is, ionomer resin covers and balata rubber covers. For simplicity, the thread wound golf balls having a cover of ionomer resin are referred to as wound ionomer balls while the thread wound golf balls having a cover of balata rubber are referred to as wound balata balls. They have advantages and disadvantages. The wound ionomer balls are superior in flying distance when struck with the driver, but considerably inferior in spin 25 properties in the approach play on the green, that is, stoppage on the green. The wound balata balls are less durable, for example, in that their cover at the ball surface can be scuffed or fretted by bunker shots and cut when topped with iron clubs.

For the purpose of improving spin property and durability, a wound golf ball using a softer ionomer resin as the cover was also proposed. This ball has problems that it has little difference in the flying distance associated with the driver from the conventional wound golf balls and that it can be cut in the cover when topped with iron clubs as are the wound balata balls.

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It would be desirable to provide a wound golf ball which is satisfactory in flying distance and spin property and is fully durable.

The present invention relates to a thread wound golf ball having a center ball, thread rubber, and a cover. The cover has a multi-layer structure including an outer layer and an inner layer. The inner layer has a higher hardness than the outer layer. The outer layer has a radial

thickness of 0.4 mm or more. Our work shows that such a ball may attain a flying distance at least comparable to that of the conventional wound ionomer balls having a cover of high hardness ionomer resin. Its spin property may compare with that of the conventional wound balata balls. Its cover is not readily cut when topped with iron clubs. 15

Although two-piece solid golf balls having a cover of two-layer structure are known in the art as disclosed in Japanese Patent Application Kokai (JP-A) Nos. 80469/1985 and 290969/1986 and EP 577,058, a two-layer cover has never been proposed for wound golf balls. The thread wound golf ball having a cover of the above-defined layer structure as proposed herein may afford the following advantages. Since the cover outer layer has a lower hardness or adequate softness, the ball gains a high spin rate and offers good spin properties and controllability on 25 approach shots. Since the cover inner layer has a higher hardness, the cover as a whole offers good repulsion or restitution, an increased initial velocity with a low spin rate, and an increased flying distance on driver shots. A combination of the outer layer having a lower hardness with 30 the inner layer having a higher hardness improves cut resistance and hence, durability. The outer layer formed of an ionomer resin having a lower hardness has higher scuffing resistance and hence, more durable than the balata covers and high hardness ionomer resin covers. 35

According to the present invention, there is provided a wound golf ball comprising a center ball, a thread rubber layer, and a cover wherein the cover has a multi-layer

structure including an outer layer having a thickness of at least 0.4 mm and an inner layer having a hardness higher than that of the outer layer.

BRIEF DESCRIPTION OF THE DRAWINGS

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The only figure, FIG. 1 is a schematic cross-sectional view of one exemplary wound golf ball.

10 Referring to FIG. 1, a wound golf ball is illustrated as comprising a spherical center ball 1. Thread rubber is wound on the center ball 1 to form a thread rubber layer 2, which is enclosed in a cover 3. According to the invention, the cover 3 has a multi-layer structure,

15 typically a two layer structure consisting of a radially outer layer 4 and a radially inner layer 5.

Each of the outer and inner layers 4 and 5 may be formed of a composition comprising a well-known cover resin such as ionomer resins and balata rubber and conventional amounts of optional additives including pigments such as titanium white and dispersants such as magnesium stearate. The outer layer has a first hardness which is relatively low and the inner layer has a second hardness which is higher than the first hardness.

The outer layer is preferably with a Shore D hardness of 40 to 55, more preferably 45 to 51. Useful resins are ionomer resins, for example, Himlan® 8120, 8220 and 8320 commercially available from MitsuiduPont Polychemical K.K. and mixtures of two or more of them, as well as balata rubber.

The inner layer is preferably formed of a resin having a Shore D hardness of 55 to 68, more preferably 60 to 66.

Useful resins are ionomer resins, for example, Himilan 1554, 1555, 1601, 1702, 1705, and 1706 commercially available from Mitsui-duPont Polychemical K.K. and mixtures of two or more of them.

:)

The difference in hardness between the inner and outer layer resins should preferably be at least 5, especially at least 10 in Shore D hardness.

According to the present invention, the outer layer

should have a radial thickness of at least 0.4 mm,

preferably 0.4 to 3.0 mm, more preferably 0.4 to 2.0 mm.

It is recommended that the outer and inner layers have a

total thickness of 1.0 to 4.0 mm, especially 1.5 to 2.5 mm.

If the total thickness is less than 1.0 mm, the cover may

be less durable against topping. If the total thickness is

beyond 4.0 mm, the ball may be sometimes low in initial

velocity. An outer layer of less than 0.4 mm fails to

provide spin properties on approach shots. The ratio of

the outer layer thickness to the inner layer thickness is

desirably from 3:7 to 7:3.

The wound golf ball of the invention may have either a liquid center or a solid center, which are both conventional. The liquid center typically consists of a rubber or center bag filled with a liquid. The rubber or center bag may be formed of any well-known composition. Water is the preferred liquid. The fill liquid preferably has a specific gravity of at least 0.9, more preferably 1.0 to 1.5, most preferably 1.0 to 1.2. Fine powder, surfactant or the like may be added to water for adjusting the specific gravity. The fine powder used herein is one 25 which consists of fine particles and is not dissolved in water. Typical examples are fillers such as barium sulfate, zinc oxide, and silica. The powder preferably has a mean particle size of 0.02 to 100 μm , especially 0.5 to The powder may be blended in an amount of 4 to 60% 30 by weight, especially 10 to 50% by weight of the fill liquid. Exemplary surfactants are dodecylbenzenesulfonic acid and sodium dodecylbenzenesulfonate. Water is the preferred liquid. The rubber or center bag may be formed of any well-known composition. Also the solid center may be of a well-known composition.

The center ball preferably has an outer diameter of 27 to 32 mm and a weight of 15.0 to 23.0 g, especially 17.5 to $21.5 \, \mathrm{g}$.

The type of thread rubber wound on the center ball and the winding technique may be conventional.

After a core is formed by winding a thread rubber layer on the center ball, any desired technique may be used in enclosing the core in a cover of multi-layer structure. For example, each covering composition is directly injection molded around the core. Alternatively, a pair of hemispherical cups are formed from each covering composition and the core is surrounded by the dual cups, which is press molded at 110 to 160°C for about 2 to 10 minutes.

The golf ball is typically made with a diameter and weight meeting the Golf Association Standards, that is, a diameter of at least 42.67 and a weight of up to 45.92 g.

EXAMPLE

20 Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples 1-5 and Comparative Examples 1-5

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A liquid center was prepared by molding a rubber composition of the formulation shown in Table 1 in a hemispherical mold cavity and vulcanizing it to form hemispherical shells. A pair of shells were mated to form a rubber bag which was filled with water. The center ball had an outer diameter of 29 mm and a weight of 18.8 g.

Table 1

		Center bag A
	Composition (pbw)	•
	Natural rubber	100
35	Stearic acid	· 1
	Zinc oxide	330
	Processing oil	30

Vulcanization promoter	1.5
Sulfur	2.5
Physical properties as vulcanized	
Hardness, JIS A scale	60
condific gravity	2.27
Bag gage, mm	2.2

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Thread rubber was wound on the liquid center ball by a conventional winding technique to form a thread rubber layer of about 6 mm thick.

Each cover composition was prepared by blending 100 parts by weight of a resin as shown in Table 2 with 5 parts by weight of titanium oxide and 0.3 parts by weight of magnesium stearate in a twin screw extruder. The cover composition was molded into hemispherical cups.

Table 2

		Cove	r com	posit	ion
	Ionomer resin (pbw)			<u>R3</u>	
20	H1557 (Zn)	25	-	-	
20	S8120 (Na)	50	-	-	-
	S8320 (Na)	_	65	90	
	H1605 (Zn)	-	-	- 10	50
	H1650 (Zn)		35	10	- 50
25	H1706 (Zn)	- 25	-	_	_
	H1856 (Na)	25 51	47	41	64
	Cover resin hardness (Shore D)	71	2,		

A wound golf ball was prepared by combining a pair of cups of one type with a pair of cups of another type in concentric overlap, mating a pair of dual cups so as to enclose the core therein, and compression molding the cups to form a cover.

Each of the thus prepared golf balls was tested for carry, total distance (carry + run), spin, and elevation angle by hitting with the driver and sand wedge. The results are shown in Table 3. The ball was also examined

-7-

for cut durability by hitting with the sand wedge at a head speed (HS) of 36 m/s.

				Table	7	1000	elumex# oviterrement	nole		
	,-	Example 7	m	4	5	Compara	2	3	4	ഹി
Structure Structure Outer layer (Shore D) R1 Inner layer (Shore D) R4 Thickness (mm) 1.8	2 layer R1 (51) R4 (64) 1.8		1	2 layer R1 (51) R4 (64) 1.8 3:7	2 layer R1 (51) R4 (64) 1.8	l layer R1 (51) R1 (51) 1.8	1 layer R4 (64) R4 (64) 1.8	2 layer R4 (64) R1 (51) 1.8 5:5	2 layer R1 (51) R4 (64) 0.8 4:6	balata (48) (48) 1.8
Thickness rated Performance W#1, HS = 45 m/s Carry (m) Total distance (m) Spin (rpm)	211.5 228.9 2880	210.7 228.4 2910	210.5 228.1 2990	211.6 229.1 2860 11.5	210.6 228.2 2950 11.5	209.7 226.5 3070 11.7	211.7 229.3 2830 11.5	211.6 229.2 2840 11.5	211.1 228.5 2900 11.5	209.5 226.1 3100 11.8
Elevation angle (') w#1, HS = 50 m/s Carry (m) Total distance (m) Spin (rpm)	. 0 & &	240.8 257.8 2800	240.8 256.0 2860 11.5	241.0 258.4 2760 11.4	240.7 257.5 2820 11.4	240.7 255.1 3000 11.6	241.4 258.5 2710 11.4	241.2 258.4 2720 11.4	240.7 257.7 2810 11.4	240.1 254.8 3050 11.7
Elevation angle () SW, HS = 20 m/s	- U	6250	6480	6130	6240	6250	4570	4590	6050	6300
Spin (Lpm) Cut durability*² SW, HS = 36 m/s		;	1	ı	1	8/30	0/30	1	30/30	1
*1 Thickness ratio is *2 The number of ball	s is outer salls with	layer	thickness/inner failure or ball	s/inner or ball	layer thickness. distortion from	thickness.	sphericity	ty		

It is evident that the wound golf balls embodying the invention are improved in flying distance and spin property and are fully durable.

Japanese Patent Application No. 201389/1994 and No. 333025/1994 is incorporated herein by reference.

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Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

CLAIMS:

1. A wound golf ball comprising a center ball, thread rubber wound thereon, and a cover enclosing the wound center, wherein

said cover has a multi-layer structure including an outer layer having a first hardness and a thickness of at least 0.4 mm and an inner layer having a second hardness higher than the first hardness.

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2. A wound golf ball of claim 1 wherein the outer and inner layers of said cover have a total thickness of 1.0 to 4.0 mm and the outer layer has a thickness of 0.4 to 3.0 mm.

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- 3. A wound golf ball of claim 1 or 2 wherein the outer layer of said cover is formed of a first resin having a Shore D hardness of 40 to 55, and the inner layer is formed of a second resin having a Shore D hardness of 55 to 68, the difference in hardness between the first and second resins being at least 5 in Shore D hardness.
- 4. A wound golf ball of any one of claims 1 to 3 wherein said center ball has an outer diameter of 27 to 32 mm and a weight of 15.0 to 23.0 g.
- 5. A wound golf ball of any one of claims 1 to 4 wherein said center ball is a liquid center.
- 6. A wound golf ball substantially as any described herein with reference to Examples 1 to 5.





Application No: Claims searched: GB 9515947.1

1-6

Examiner:

David Whitfield

Date of search:

19 September 1995

Patents Act 1977

Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

C3M MXC UK CI (Ed.N): A6D DIA DIB C3V VEM

Int CI (Ed.6): A63B 37/12

ONLINE:- WPI Other:

Documen:s considered to be relevant:

Category	luentity of docume	ent and relevant passag	;e				Relevant to claims
X:E	GB2280379A	(LISCO) (WHOLE	DO	CU	ME	NT)	1,4,5
х	GB 2064338A	(BRIDGESTONE)	(••	•)	•
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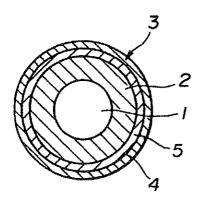
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(54) Wound golf ball

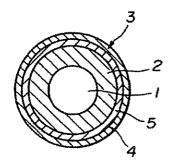
(57) In a wound golf ball comprising a solid center (1), thread rubber (2), and a cover (3), the cover has a multilayer structure including an outer layer (4) and an inner layer (5) having a higher hardness than the outer layer. The outer layer (4) is 0.4 - 3.0 mm thick. The ball affords improved spin and durability.

FIG.1



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FIG.1



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Wound Golf Ball

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This invention relates to a thread wound golf ball having good spin property and durability.

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Prior art thread wound golf balls with a solid center have two types of covers, that is, ionomer resin covers and balata rubber covers. For simplicity, the thread wound golf balls having a cover of ionomer resin are referred to as wound ionomer balls while the thread wound golf balls having a cover of balata rubber are referred to as wound balata balls. They have advantages and disadvantages. The wound ionomer balls are superior in flying distance when struck with the driver, but considerably inferior in spin properties in the approach play on the green, that is, stoppage on the green. The wound balata balls are less durable, for example, in that their cover at the ball surface can be scuffed or fretted by bunker shots and cut when topped with iron clubs.

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For the purpose of improving spin property and durability, a wound golf ball using a softer ionomer resin as the cover was also proposed. This ball has problems that it has little difference in the flying distance associated with the driver from the conventional wound golf balls and that it can be cut in the cover when topped with iron clubs as are the wound balata balls.

It would be desirable to provide a wound golf ball which is satisfactory in flying distance and spin property and has good durability.

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The present invention relates to a thread wound golf ball having a solid center, thread rubber, and a cover. The cover has a multi-layer structure including an outer layer and an inner layer. The inner layer has a higher hardness than the outer layer. The outer layer has a radial thickness of 0.4 mm or more. Our work shows that such a ball may attain a flying distance at least comparable to that of the conventional wound ionomer balls having a cover of high hardness ionomer resin. Its spin property can be comparable to that of the conventional wound balata balls. Its cover is not readily cut when topped with iron clubs.

15 Although two-piece solid golf balls having a cover of two-layer structure are known in the art as disclosed in Japanese Patent Application Kokai (JP-A) Nos. 80469/1985 and 290969/1986 and EP 577,058, a two-layer cover has never 20 been proposed for wound golf balls. The thread wound golf ball having a solid center and a cover of the above-defined layer structure as proposed herein may afford the Since the cover outer layer has following features. a lower hardness or adequate softness, the ball gains a high spin rate and offers good spin properties and 25 controllability on approach shots. Since the cover inner layer has a higher hardness, the cover as a whole offers good repulsion or restitution, an increased initial velocity with a low spin rate, and an increased flying distance on driver shots. A combination of the outer layer 30 having a lower hardness with the inner layer having a higher hardness improves cut resistance and hence, durability. The outer layer formed of an ionomer resin having a lower hardness has higher scuffing resistance and hence, more durable than the balata covers and high 35

According to the present invention, there is provided a wound golf ball comprising a solid center, a thread

hardness ionomer resin covers.

rubber layer, and a cover wherein the cover has a multilayer structure including an outer layer having a thickness of at least 0.4 mm and an inner layer having a hardness higher than that of the outer layer.

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BRIEF DESCRIPTION OF THE DRAWINGS

The only figure, FIG. 1 is a schematic cross-sectional view of one exemplary wound golf ball.

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Referring to FIG. 1, a wound golf ball is illustrated as comprising a spherical solid center 1. Thread rubber is wound on the center 1 to form a thread rubber layer 2, which is enclosed in a cover 3. According to the invention, the cover 3 has a multi-layer structure, typically a two layer structure consisting of a radially outer layer 4 and a radially inner layer 5.

Each of the outer and inner layers 4 and 5 may be formed of a composition comprising a well-known cover resin such as ionomer resins and balata rubber and conventional amounts of optional additives including pigments such as titanium white and dispersants such as magnesium stearate. The outer layer has a first hardness which is relatively low and the inner layer has a second hardness which is higher than the first hardness.

The outer layer is preferably formed with a Shore D hardness of 40 to 55, more preferably 45 to 51. Useful resins are ionomer resins, for example, Himilan® 8120, 8220 and 8320 commercially available from MitsuiduPont Polychemical K.K. and mixtures of two or more of them, as well as balata rubber.

The inner layer is preferably formed of a resin having a Shore D hardness of 55 to 68, more preferably 60 to 66. Useful resins are ionomer resins, for example, Himilan 1554, 1555, 1601, 1702, 1705, and 1706 commercially available from Mitsui-duPont Polychemical K.K. and mixtures of two or more of them.

The difference in hardness between the inner and outer layer resins should preferably be at least 5, especially at least 10 in Shore D hardness.

According to the present invention, the outer layer should have a radial thickness of at least 0.4 mm, especially 0.4 to 3.0 mm. An outer layer of less than 0.4 mm fails to provide spin properties on approach shots. A ball with an outer layer of more than 3.0 mm May be less repulsive and afford a shorter flying distance.

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It is recommended that the outer and inner layers have a total thickness of 1.0 to 4.0 mm, especially 1.5 to 2.5 mm. The ratio of the outer layer thickness to the inner layer thickness is desirably from 3:7 to 7:3. If the total thickness is less than 1.0 mm, the cover may be less durable against topping. If the total thickness is beyond

4.0, the ball may be sometimes low in initial velocity. If the outer layer is thinner outside the above-defined ratio range, a problem may arise with respect to spin on approach shots. If the outer layer is thicker outside the above-defined ratio range, the flying distance associated with the driver may be short.

The wound golf ball of the invention has a solid center rather than a liquid center. This prevents shortening of the flying distance during play at low temperature as compared with the wound golf balls with a liquid center. The solid center preferably has an outer diameter of 27 to 38 mm, especially 29 to 35 mm. If the solid center is less than 27 mm in diameter, a ball would receive more spin, follow a rather getting-up trajectory, and fly a shorter distance against a head wind. A solid center having a diameter of more than 38 mm is too large to wound thread rubber thereon to a proper thickness so that the ball might fail to provide adequate hardness for hitting feel unless the solid center is extremely hard.

The solid center can be formed by any well-known technique. For example, a well-known rubber composition comprising base rubber and a peroxide is molded under heat and pressure to form the solid center. The base rubber may

be polybutadiene rubber or a mixture of polybutadiene rubber and polyisoprene rubber which are conventionally used in solid golf balls. In the practice of the invention, 1,4-polybutadiene rubber having more than 90% of cis-structure is preferred for higher repulsion. Cocrosslinking agents which are conventionally used in solid golf balls include zinc and magnesium salts of unsaturated fatty acids such as methacrylic acid and acrylic acid and esters such as trimethylpropane trimethacrylate. agents may be used in the rubber composition for the solid center. Zinc acrylate is most preferred because of high repulsion. Typically about 15 to 30 parts by weight of the co-crosslinking agent is blended with 100 parts by weight of the base rubber. Any well-known peroxide may be used. Preferred are dicumyl peroxide and mixtures of dicumyl peroxide and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclo-Typically about 0.5 to 1.5 parts by weight of the peroxide is blended with 100 parts by weight of the base rubber. The rubber composition may optionally contain zinc oxide and barium sulfate for specific gravity adjustment

The hardness of the solid center is not critical since it is determined by considering the feel to the player on impacts entailing great deflection as by driver hits and the head speed of the player. Most often, the solid center has a hardness of 45 to 80, especially 60 to 80 on JIS C hardness scale as measured at the solid core surface.

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and an anti-oxidant.

The type of thread rubber wound on the solid center and the winding technique may be conventional.

After a core is formed by winding a thread rubber layer on the solid center, any desired technique may be used in enclosing the core in a cover of multi-layer structure. For example, each covering composition is directly injection molded around the core. Alternatively, a pair of hemispherical cups are formed from each covering composition and the core is surrounded by the dual cups, which is press molded at 110 to 160°C for about 2 to 10 minutes.

The golf ball is typically made with a diameter and weight meeting the Golf Association Standards, that is, a diameter of at least 42.67 mm and a weight of up to 45.92 g.

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EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

10 Examples 1-7 and Comparative Examples 1-4

Each solid center was prepared by blending suitable ingredients to form a rubber composition as shown in Table 1, milling the composition in a roll mill, and press molding the composition at 155°C for 15 minutes to form a center ball.

Table 1 Solid center Composition (pbw) 100 100 100 Polybutadiene rubber 20 1 1 1 Stearic acid 20 45 30 zinc oxide 6 25 22 Lead acrylate 21 60 35 Barium sulfate 1.2 1.2 1.2 Dicumyl peroxide 25 35.3 mm 27.8 mm 31.8 mm Center outer diameter

Thread rubber was wound on the solid center by a conventional winding technique to form a thread rubber layer of about 6 mm thick.

Each cover composition was prepared by blending 100 parts by weight of a resin as shown in Table 2 with 5 parts by weight of titanium oxide and 0.3 parts by weight of magnesium stearate in a twin screw extruder. The cover composition was molded into hemispherical cups.

-7-

Table 2

		Cove	er con	posit	ion
	Ionomer resin (pbw)	<u>R1</u>	R2	R3	<u>R4</u>
	H1557 (Zn)	25	-		_
5	S8120 (Na)	50		•••	_
	S8320	***	65	90	-
	H1605 (Zn)		***	-	50
	H1650	***	35	10	-
	H1706 (Zn)	**	****	<u>.</u> .	50
10	H1856 (Na)	25		-	-
	Cover resin hardness(Shore D)	51	47	41	64

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A wound golf ball was prepared by combining a pair of cups of one type with a pair of cups of another type in concentric overlap, mating a pair of dual cups so as to enclose the core therein, and compression molding the cups to form a cover.

Each of the thus prepared golf balls was tested for carry, total distance (carry + run), spin, and elevation angle by hitting with the driver and sand wedge. The results are shown in Table 3. The ball was also examined for cut durability by hitting with the sand wedge at a head speed (HS) of 36 m/s.

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ative Ex	2		_	23.4	0	,					1.8	:				, c.c.		07/7	11.6		44		5 F	0107	-	4570) }	00/0	06/0				
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	<u> </u>	2	;	3. t.	23.4	1.91		37.6	7.	7 7 7 7 1	*	æ :	5:5		•	213.0	231.1	2890	1117	, , , ,	!	43.	50	2760	,	1	6340		1		solid center under a	ckness/J	TO SINII
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			Solid center	Outer diameter (mm)	Weight (a)	Hardness* (mm)	Country	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Structure	Outer layer (Shore D)	Inner layer (Shore D)	Thickness (mm)	Thickness ratio*2	Performance	W#1, HS = 45 m/s	Carry (m)	50+41 Juintance (E)	ייין פייין פיייין פיייין פייין פייין פייין פיייין פיייין פייין פיייין פייין פי	Spin (rpm)	Elevation angle (")	W#1, HS = 50 m/s	Carry (m)	HOTEL TINE	Coin (rom)	Flevation angle (°)	SW, HS = 20 m/s	Spin (rpm)	Cut durability*	S/m 36 m/s		*1 Hardness is a defi	+2 Thickness ratio is outer layer thickness/inner	*3 The number of Dal.

It is evident that the wound golf balls embodying the invention are improved in spin property and durability.

Japanese Patent Application No. 201389/1994 and No. 334564/1994 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

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CLAIMS:

 A wound golf ball comprising a solid center, thread rubber wound thereon, and a cover enclosing the wound center, wherein

said cover has a multi-layer structure including an outer layer having a first hardness and a thickness of at least 0.4 mm and an inner layer having a second hardness higher than the first hardness.

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- 2. A wound golf ball of claim 1 wherein the outer layer of said cover is formed of a first ionomer resin having a Shore D hardness of 40 to 55, and the inner layer is formed of a second ionomer resin having a Shore D hardness of 55 to 68, the difference in hardness between the first and second ionomer resins being at least 5 in Shore D hardness.
 - 3. A ball of claim 1 or claim 2 wherein the outer and inner layers have a total thickness of 1.0 to 4.0 mm and the ratio of the outer layer thickness to the inner layer thickness is from 3:7 to 7:3.
 - 4. A ball of any preceding claim wherein said solid center has an outer diameter of 27 to 38 mm.
 - 5. A wound golf ball substantially as any described herein with reference to Examples 1 to 7.





Application No: Claims searched: GB 9515967.9

1-5

Examiner:
Date of search:

David Whitfield 19 September 1995

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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x	GB2064338	(BRIDGESTONE)	(*	**)	
Х	WO80/01541AI	(QUESTOR)	(a	**)	

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